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(54) Title: HYDROPHILIC POLYMERS, PRESSURE SENSITIVE ADHESIVES AND COATINGS

(57) Abstract: A method for the preparation of gel-free polymers in alcohol, in water, and in solutions of alcohol and water. The polymers produced by the method of the invention are useful as hydrophilic pressure sensitive adhesives, coatings, hydrogels, films, topical compositions, cosmetic compositions, transdermal drug delivery systems, and carrier for a mucus membrane drug delivery systems.

## HYDROPHILIC POLYMERS, PRESSURE SENSITIVE ADHESIVES AND COATINGS

### FIELD OF THE INVENTION

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This invention is related to methods of preparing hydrophilic homopolymers and copolymers and to their use as pressure sensitive adhesives, hydrogels, coatings, films, and compositions suitable for topical application to the skin.

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### BACKGROUND OF THE INVENTION

The family of synthetic hydrophilic polymers includes polyacrylic acid, polyvinyl pyrrolidone, polyvinyl alcohol, polyacrylamide, poly hydroxybutyl acrylate, and poly 2-hydroxyethyl methacrylate. In this family of synthetic  
15 hydrophilic polymers, poly 2-hydroxyethyl methacrylate and poly hydroxybutyl acrylate are water insoluble polymers prepared from a water soluble monomer. The other mentioned polymers require crosslinking to form a water insoluble polymer.

2-Hydroxyethyl methacrylate polymers are of interest because of their  
20 biocompatibility as evidenced by excellent performance in animal implant studies. The extensive use of 2-hydroxyethyl methacrylate polymers for contact lenses for the eyes illustrates the non irritating nature of the polymers.

Other than commercial use in contact lenses, 2-hydroxyethyl methacrylate  
25 polymers have had limited commercial success, used at low percentages only, because of the nature of the monomer. Industrial grade 2-hydroxyethyl methacrylate monomer contains a small amount of crosslinker impurity which can cause gel formation during solvent polymerization. The 2-hydroxyethyl methacrylate monomer is water soluble and, as mentioned above, the 2-  
30 hydroxyethyl methacrylate polymer is water insoluble, which causes difficulty in emulsion polymerization employing a high portion of 2-hydroxyethyl methacrylate

monomer. The preparation of 2-hydroxyethyl methacrylate polymer, therefore, generally requires the use of very pure and expensive monomer or a very extensive and expensive polymerization process.

5           Requirements of high quality inkjet coatings include clarity, water resistance, good ink absorption with quick drying, and low surface friction to enhance sheet feeding in inkjet printers. Typical inkjet coatings satisfy the requirements of water resistance, good ink absorption with quick drying, and low surface friction through the use of mixtures of polymers, or polymers with pigments, however, these  
10   mixtures are not clear.

U.S. Patent 2,976,576 describes the use of poly 2-hydroxyethyl methacrylate resin for contact lenses and body implants.

15           U.S. Patent 3,220,960 describes the use of poly 2-hydroxyethyl methacrylate resin for contact lenses and body implants.

U.S. Patent 3,567,760 describes the preparation of 2-hydroxyethyl methacrylate copolymers in methanol that are water soluble salts for entrapping  
20   drugs, pesticides, flavoring agents, and fragrances.

U.S. Patent 3,963,685 describes the preparation of methanol soluble poly 2-hydroxyethyl methacrylate for wound care dressings using high purity 2-hydroxyethyl methacrylate monomer having not over 0.035 weight percent of  
25   alkylene glycol dimethacrylate impurities.

EP 024164A1 describes the preparation of methanol soluble poly 2-hydroxyethyl methacrylate using high purity 2-hydroxyethyl methacrylate monomer.

Polymer International, vol. 36 no. 4, pp.303-308 (April 1995), describes the preparation of dimethylformamide soluble poly 2-hydroxyethyl methacrylate using a chain transfer agent to prevent gellation.

5 U.S. Patent 4,303,066 describes the use of a plasticized poly 2-hydroxyethyl methacrylate resin prepared from high purity monomer as a non-tacky synthetic film for skin burns, with shortened forming time by adding water to the mixture.

10 U.S. Patent 4,593,053 describes the use of a plasticized polyvinyl pyrrolidone as a hydrophilic medical type pressure sensitive adhesive for biomedical electrodes and transdermal devices.

15 WO 92/11825 describes the use of plasticized poly 2-hydroxyethyl methacrylate resin as a hydrophilic medical type pressure sensitive adhesive for a medical device.

20 U.S. Patent 5,225,473 describes the use of a UV cured, plasticized polyvinyl pyrrolidone as a hydrophilic medical type pressure sensitive adhesive for biomedical electrodes and transdermal devices.

U.S. Patent 4,892,787 describes coated paper for inkjet printing containing pigment, an acrylic emulsion, and a water soluble polymer.

25 U.S. Patent 5,206,071 describes acrylic graft copolymers and water soluble polymers.

U.S. Patent 5,478,631 describes an inkjet recording sheet using a pigment and an amphoteric ion latex.

30 EP 0716929A1 describes acrylic graft copolymers and water soluble polymers.

DE 19516111A1 describes water soluble copolymers with crosslinkers.

U.S. Patent 5,672,392 describes the preparation of recording materials for inkjet printers using acrylic emulsions and water soluble polymers.

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U.S. Patent No. 3,813,695 discloses a rubber or latex surgical glove that is laminated with an internal plastic lining of a hydrophilic material.

U.S. Patent No. 4,575,476 discloses a dipped rubber glove having an outer  
10 rubber layer and a lubricating layer formed of a hydrogel polymer bonded thereto to provide a skin-contacting surface of the glove.

In general, the present invention is directed to providing a cost-effective method for the preparation of hydrophilic homopolymers and copolymers with  
15 utility as films, coatings, pressure sensitive adhesives, and compositions suitable for topical application to the skin.

The present invention is further directed to providing clear inkjet coatings without pigments that are water resistant and have good ink absorption with quick  
20 drying times.

#### BRIEF SUMMARY OF THE INVENTION

A method is provided for the preparation of gel-free poly 2-hydroxyethyl  
25 methacrylate substantially in the absence of a chain transfer agent, comprising introducing monomeric 2-hydroxyethyl methacrylate containing ethylene glycol dimethacrylate impurities in the range of no more than about 0.05-0.1% by weight of the monomer, into alcohol, polymerizing the 2-hydroxyethyl methacrylate to form a polymerization mixture, and optionally removing the alcohol. The alcohol is  
30 preferably selected from one of methanol and ethanol. Hydrophilic pressure sensitive adhesives are provided by adding polyethylene glycol to the polymerization

mixture prior to removing the alcohol. Flexible hydrophilic coatings also are provided by adding glycerin to the polymerization mixture prior to removing the alcohol by drying.

5           In another embodiment, the monomeric 2-hydroxyethyl methacrylate contains alkylene glycol methacrylate impurities in the range of no more than about 3% by weight, wherein the alkylene glycol methacrylate impurities are selected from the group consisting of ethylene glycol dimethacrylate, diethylene glycol monomethacrylate, methacrylic acid and mixtures thereof.

10

A method is also provided for the preparation of a gel free, hydrophilic, water soluble polymer substantially in the absence of a chain transfer agent comprising a copolymer of 2-hydroxyethyl methacrylate and acrylic acid or methacrylic acid, including introducing monomeric 2-hydroxyethyl methacrylate  
15 into water solution with one of acrylic acid and methacrylic acid, adjusting the pH of the solution to a pH in the range of greater than about pH 3 to less than about pH 9, and copolymerizing the monomeric 2-hydroxyethyl methacrylate and acrylic or methacrylic acid.

20           In one embodiment, the monomeric 2-hydroxyethyl methacrylate contains at least 0.05% by weight, based on the monomer, of ethylene glycol dimethacrylate.

In another embodiment, hydrogels are prepared with copolymer concentrations greater than about 35% by weight.

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In another embodiment, the copolymer of 2-hydroxyethyl methacrylate and acrylic acid or methacrylic acid is blended with a polyalkylene glycol, such as polyethylene glycol, to form a pressure sensitive adhesive.

30           In another embodiment, the copolymer of 2-hydroxyethyl methacrylate and acrylic acid or methacrylic acid is blended with glycerin to form a flexible coating.

A method is also provided for the preparation of a gel free hydrophilic polymer substantially in the absence of a chain transfer agent comprising a copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate, including introducing monomeric 2-hydroxyethyl methacrylate containing no more than about 5 0.05-0.1% by weight of ethylene glycol dimethacrylate into an alcohol solution with 4-hydroxybutyl acrylate, polymerizing the 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate to form a polymerization mixture, and removing the alcohol. The alcohol is preferably selected from one of methanol and ethanol, with ethanol being preferred.

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In another embodiment, the monomeric 2-hydroxyethyl methacrylate contains no more than about 3% by weight alkylene glycol methacrylate impurities, wherein the alkylene glycol methacrylate impurities are selected from the group consisting of ethylene glycol dimethacrylate, diethylene glycol monomethacrylate, 15 methacrylic acid and mixtures thereof.

A method of preparing an acrylic emulsion ink jet receptive clear coating is also provided comprising: forming an alkyl acrylate monomer-containing pre-emulsion feed mixture, introducing an activator into the alkyl acrylate monomer-containing pre-emulsion feed mixture, reacting a water soluble monomer feed in 20 said alkyl acrylate monomer-containing pre-emulsion feed mixture, said water soluble monomer feed comprising 2-hydroxyethyl methacrylate and n-vinylpyrrolidone, to form a clear polymer in said alkyl acrylate monomer-containing pre-emulsion feed mixture.

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In another embodiment, the method further comprises subsequently reacting with said clear polymer in said alkyl acrylate monomer-containing pre-emulsion feed mixture, a water insoluble monomer feed mixture comprising 2-hydroxyethyl methacrylate, n-vinyl pyrrolidone, butyl acrylate, and methacrylic acid to form a 30 clear polymer over said polymer in said alkyl acrylate monomer-containing pre-emulsion feed mixture.

A method for the preparation of a powdered low gel poly 2-hydroxyethyl methacrylate substantially in the absence of a chain transfer agent is also provided comprising: introducing monomeric 2-hydroxyethyl methacrylate containing ethylene glycol dimethacrylate impurities in the range of no more than about 0.05 to about 0.1% by weight, based on the monomer, into water, polymerizing the 2-hydroxyethyl methacrylate, drying said polymerized the 2-hydroxyethyl methacrylate, and grinding said dried polymerized 2-hydroxyethyl methacrylate to form a powder.

10 In another embodiment, the monomeric 2-hydroxyethyl methacrylate contains no more than about 3% by weight alkylene glycol methacrylate impurities, wherein the alkylene glycol methacrylate impurities are selected from the group consisting of ethylene glycol dimethacrylate, diethylene glycol monomethacrylate, methacrylic acid and mixtures thereof...

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In another embodiment, said poly 2-hydroxyethyl methacrylate powder is blended with a polyalkylene glycol, such as polyethylene glycol to form a pressure sensitive adhesive.

20 A method is also provided for the preparation of a gel free hydrophilic polymer substantially in the absence of a chain transfer agent comprising a copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate, including introducing monomeric 2-hydroxyethyl methacrylate containing no more than about 0.05-0.1% by weight of ethylene glycol dimethacrylate into an alcohol solution with 4-hydroxybutyl acrylate, polymerizing the 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate to form a polymerization mixture, and removing the alcohol. The alcohol is selected from one of methanol and ethanol, with ethanol being preferred.

30 In another embodiment, the monomeric 2-hydroxyethyl methacrylate contains no more than about 3% by weight alkylene glycol methacrylate impurities,



wherein the alkylene glycol methacrylate impurities are selected from the group consisting of ethylene glycol dimethacrylate, diethylene glycol monomethacrylate, methacrylic acid and mixtures thereof.

5           A method is also provided for the preparation of a gel free hydrophilic copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate substantially in the absence of a chain transfer agent comprising introducing monomeric 2-hydroxyethyl methacrylate containing no more than about 0.05-0.1% by weight of ethylene glycol dimethacrylate into a solution of water and alcohol with 4-  
10   hydroxybutyl acrylate, and polymerizing the 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate to form a polymerization mixture.

In a preferred embodiment, the alcohol is selected from one of methanol and ethanol, with ethanol being preferred.

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In another embodiment, the monomeric 2-hydroxyethyl methacrylate contains no more than about 3% by weight alkylene glycol methacrylate impurities, wherein the alkylene glycol methacrylate impurities are selected from the group consisting of ethylene glycol dimethacrylate, diethylene glycol monomethacrylate,  
20   methacrylic acid and mixtures thereof.

In another embodiment, the copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate is blended with a polyalkylene glycol, such as polyethylene glycol, to form a pressure sensitive adhesive.

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In another embodiment, the present invention provides a method for the preparation of a gel free hydrophilic homopolymer of 2-hydroxyethyl methacrylate substantially in the absence of a chain transfer agent comprising introducing monomeric 2-hydroxyethyl methacrylate containing no more than about 0.05-0.1%  
30   by weight of ethylene glycol dimethacrylate into a solution of water and alcohol, and polymerizing the 2-hydroxyethyl methacrylate.

In a preferred embodiment, the alcohol is selected from one of methanol and ethanol, with ethanol being preferred. These homopolymers of 2-hydroxyethyl methacrylate prepared are stable in solution.

5 In another embodiment, the monomeric 2-hydroxyethyl methacrylate contains no more than about 3% by weight alkylene glycol methacrylate impurities, wherein the alkylene glycol methacrylate impurities are selected from the group consisting of ethylene glycol dimethacrylate, diethylene glycol monomethacrylate, methacrylic acid and mixtures thereof.

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The invention also provides a method for the preparation of a gel-free homopolymer of 4-hydroxybutyl acrylate substantially in the absence of a chain transfer agent comprising introducing monomeric 4-hydroxybutyl acrylate into alcohol, and polymerizing the 4-hydroxybutyl acrylate to form a polymerization  
15 mixture.

In another embodiment, the present invention provides a method for the preparation of a gel free hydrophilic homopolymer of 4-hydroxybutyl acrylate substantially in the absence of a chain transfer agent comprising introducing  
20 monomeric 4-hydroxybutyl acrylate into a solution of water and alcohol, and polymerizing the 4-hydroxybutyl acrylate.

In a preferred embodiment, the alcohol is selected from one of methanol and ethanol, with ethanol being preferred.

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#### DETAILED DESCRIPTION OF THE INVENTION

In one embodiment, the present invention provides a method for the preparation of a gel-free poly 2-hydroxyethyl methacrylate substantially in the  
30 absence of a chain transfer agent. The method includes introducing monomeric 2-hydroxyethyl methacrylate containing ethylene glycol dimethacrylate impurities in

the range of no more than about 0.05 to 0.1% by weight into an alcohol selected from one of methanol and ethanol, polymerizing the 2-hydroxyethyl methacrylate to form a polymerization mixture, and removing the alcohol. Polymerization is induced by free radical initiation, and the alcohol is preferably removed by coating a substrate and drying the mixture. In one embodiment, the monomeric 2-hydroxyethyl methacrylate contains alkylene glycol impurities in a total amount of no more than 3% by weight, and the impurities are selected from the group consisting of ethylene glycol dimethacrylate, diethylene glycol monomethacrylate, methacrylic acid and mixtures thereof. The controlled level of impurities results in the gel free polymer, even without using ultra-pure monomer.

As described above, free radical polymerization is initiated by a suitable initiator. The initiator must be soluble in the alcohol and the 2-hydroxyethyl methacrylate monomer mixture. Suitable initiators that are soluble in alcohol include, but are not limited to, peroxides such as benzoyl peroxide, and azo compounds, such as 2,2'-azobis(isobutyronitrile).

The method of the present invention, therefore, provides for the cost effective preparation of a gel-free poly 2-hydroxyethyl methacrylate, substantially in the absence of a chain transfer agent, using industrial grade 2-hydroxyethyl methacrylate monomer. A 2-hydroxyethyl methacrylate monomer suitable for use in the method of the present invention is available from Mitsubishi Rayon, Japan.

In another embodiment, the present invention provides a method for the preparation of a gel-free poly 2-hydroxyethyl methacrylate substantially in the absence of a chain transfer agent, to achieve a hydrophilic pressure sensitive adhesive. The method includes introducing monomeric 2-hydroxyethyl methacrylate containing ethylene glycol dimethacrylate impurities in the range of about 0.05 to 0.1% by weight into an alcohol selected from one of methanol or ethanol, polymerizing the 2-hydroxyethyl methacrylate to form a polymerization mixture, adding a polyalkylene glycol, such as polyethylene glycol in a range of about 40%

to about 70% by weight, based on the weight of the polymer and the polyethylene glycol, and removing the alcohol to form a hydrophilic pressure sensitive adhesive. Polymerization is induced by free radical initiation, and alcohol removal is preferably accomplished by coating the mixture onto a substrate and drying the mixture. Although the preferred polyalkylene glycol used to prepare the pressure sensitive is polyethylene glycol, other polyalkylene glycols, such as polypropylene glycol may be used. In addition, copolymers of ethylene and propylene glycol may also be used to form the pressure sensitive adhesive.

10 In another embodiment, the 2-hydroxyethyl methacrylate contains alkylene glycol impurities in a total amount of no more than about 3% by weight of monomer, and the impurities are selected from the group consisting of ethylene glycol dimethacrylate, diethylene glycol monomethacrylate, methacrylic acid and mixtures thereof. The hydrophilic pressure sensitive adhesives formed by this method have utility in many label and tape applications, and is particularly suitable for medical applications.

In yet another embodiment, the present invention provides a method for the preparation of a flexible hydrophilic coating comprising a gel-free poly 2-hydroxyethyl methacrylate produced substantially in the absence of a chain transfer agent. The method comprises introducing monomeric 2-hydroxyethyl methacrylate containing ethylene glycol dimethacrylate impurities in the range of about 0.05 to 0.1% by weight into an alcohol selected from one of methanol and ethanol, polymerizing the 2-hydroxyethyl methacrylate to form a polymerization mixture, adding glycerin to the polymerization mixture in an amount from about 10% to about 50% by weight of the polymer, preferably about 25% by weight of the polymer, and removing the alcohol to form a flexible hydrophilic coating. Polymerization is induced by free radical initiation, and alcohol removal by coating the mixture and drying.

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In another embodiment, the 2-hydroxyethyl methacrylate contains alkylene glycol methacrylate impurities in the range of about 3%, based on the weight of the monomer. Preferably, the alkylene glycol impurities are selected from the group consisting of ethylene glycol dimethacrylate, diethylene glycol monomethacrylate, methacrylic acid and mixtures thereof, in a total amount of no more than about 3% by weight of monomer. The flexible hydrophilic coating formed by this method has utility in skin-friendly applications in which a high Moisture Vapor Transmission Rate (MVTR) is needed together with protective, skin barrier properties. The coating is also suitable for printable coatings, such as inkjet coatings for paper, plastic film, and the like.

While the above methods involve the formulation of a homopolymer of the 2-hydroxyethyl methacrylate monomer, the present invention also provides a method for the preparation of a gel free, hydrophilic, water soluble polymer comprising a copolymer of 2-hydroxyethyl methacrylate and acrylic acid or methacrylic acid. This method includes introducing monomeric 2-hydroxyethyl methacrylate into water solution with one of acrylic acid and methacrylic acid in weight ratio in the range of about 3 to about 15%, adjusting the pH of the solution to a pH in the range of greater than about pH 3 to less than about pH 9, and copolymerizing the monomeric 2-hydroxyethyl methacrylate and acrylic or methacrylic acid. Copolymerization is induced by free radical initiation. A pH of 3 or less and a pH of 9 or greater should be avoided, because the reactants may precipitate out or not form a useable copolymer.

In one preferred embodiment, the method of forming a copolymer of 2-hydroxyethyl methacrylate and one of acrylic acid and methacrylic acid includes introducing monomeric 2-hydroxyethyl methacrylate into water solution with one of acrylic acid and methacrylic acid in weight ratio in the range of about 3 to about 15%, adjusting the pH of the solution to at least pH 5, and copolymerizing the monomeric 2-hydroxyethyl methacrylate and acrylic or methacrylic acid.

In one embodiment, the 2-hydroxyethyl methacrylate monomer contains at least 0.05% by weight of ethylene glycol dimethacrylate.

An initiator is added to the mixture of the monomeric 2-hydroxyethyl methacrylate and acrylic or methacrylic acid in an amount effective to initiate copolymerization. Suitable initiators include dissociative initiators and redox initiators. Suitable dissociative initiators that may be used in the present invention include, but are not limited to, persulfates such as ammonium persulfate, potassium persulfate and sodium persulfate, hydrogen peroxide, tert-butyl hydroperoxide, and azo compounds such as 4,4'-azobis(4-cyanovaleric acid). Redox initiators include, but are not limited to, persulfates with bisulfate, such as sodium persulfate with sodium metabisulfite, hydrogen peroxide with ferrous ion, sulfite ion, bisulfite ion or ascorbic acid, and hydroperoxides with sulfoxylates, such as tert-butyl hydroperoxide with sodium formaldehyde sulfoxylate.

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In a preferred embodiment, methacrylic acid is used. In another preferred embodiment, the hydrophilic copolymer comprises from about 90% to about 95% by weight 2-hydroxyethyl methacrylate.

In the preparation of the hydrophilic copolymer of 2-hydroxyethyl methacrylate and methacrylic acid or acrylic acid of the present invention, it is preferable to raise the pH of the monomer mixture to at least a pH of about 5 in order to neutralize the monomer mixture before polymerization to prevent the precipitation of the polymer as it is formed. The pH adjustment may be accomplished by adding aqueous ammonium hydroxide or other basic chemical(s) known to those skilled in the art. The hydrophilic copolymer that is formed is soluble in methanol and soluble in water at concentrations up to about 35% by weight. At concentrations greater than about 35% by weight in water, the hydrophilic copolymer becomes a hydrogel.

30

By definition, a hydrogel is swellable with water and insoluble in water, forms an equilibrium state with water, and maintains its equilibrium shape. The hydrophilic copolymers of 2-hydroxyethyl methacrylate and methacrylic acid or acrylic acid of this invention meet all of the criteria for a hydrogel at polymer concentrations greater than about 35% by weight without the necessity of crosslinking. Hydrogels at lower concentrations of polymer can meet this criteria with crosslinking with formaldehydes, metal salts, aziridines, isocyanates, dichromates, and the like, in the amount of up to about 10% by weight of polymer. If the copolymers are crosslinked, then the amount of crosslinker is preferably less than about 10% by weight of the polymer if crosslinkers other than isocyanates are used, and up to about 20% by weight of the polymer if isocyanates are used.

In another embodiment, the present invention provides a method for the preparation of substantially gel-free, hydrophilic, water soluble copolymers of 2-hydroxyethyl methacrylate and methacrylic acid or acrylic acid substantially in the absence of a chain transfer agent, to achieve a hydrophilic pressure sensitive adhesive. The method includes introducing monomeric 2-hydroxyethyl methacrylate into water solution with one of acrylic acid and methacrylic acid, adjusting the pH of the monomer mixture to a pH in the range of greater than about pH 3 to about less than pH 9, copolymerizing the 2-hydroxyethyl methacrylate and acrylic or methacrylic acid to form a polymerization mixture, adding a polyalkylene glycol, such as polyethylene glycol in a range of about 40% to about 70% by weight, based on the weight of the polymer and the polyethylene glycol, to the polymerization mixture, and removing the water to form a hydrophilic pressure sensitive adhesive. Polymerization is induced by free radical initiation, and water removal is preferably accomplished by coating the mixture onto a substrate and drying the mixture. Although the preferred polyalkylene glycol used to prepare the pressure sensitive is polyethylene glycol, other polyalkylene glycols, such as polypropylene glycol may be used. In addition, copolymers of ethylene and propylene glycol may also be used to form the pressure sensitive adhesive.

In one preferred embodiment, the method of forming a copolymer of 2-hydroxyethyl methacrylate and one of acrylic acid and methacrylic acid includes introducing monomeric 2-hydroxyethyl methacrylate into water solution with one of acrylic acid and methacrylic acid in weight ratio in the range of about 3 to about 5 15%, adjusting the pH of the solution to at least pH 5, and copolymerizing the monomeric 2-hydroxyethyl methacrylate and acrylic or methacrylic acid.

In yet another embodiment, the present invention provides a method for the preparation of a flexible hydrophilic coating comprising a substantially gel-free 10 hydrophilic copolymer of 2-hydroxyethyl methacrylate and methacrylic acid and acrylic acid produced substantially in the absence of a chain transfer agent. The method comprises introducing monomeric 2-hydroxyethyl methacrylate into water solution with one of acrylic acid and methacrylic acid, adjusting the pH of the monomer mixture to a pH in the range of greater than about pH 3 to about less than 15 pH 9, copolymerizing the 2-hydroxyethyl methacrylate and acrylic or methacrylic acid to form a polymerization mixture, adding glycerin to the polymerization mixture in an amount from about 10% to about 50% by weight of the polymer, preferably about 25% by weight of the polymer, and removing the water to form a flexible hydrophilic coating, which is particularly suited for medical and skin care. 20 Polymerization is induced by free radical initiation, and water removal by coating the mixture and drying.

In one preferred embodiment, the method of forming a copolymer of 2-hydroxyethyl methacrylate and one of acrylic acid and methacrylic acid includes 25 introducing monomeric 2-hydroxyethyl methacrylate into water solution with one of acrylic acid and methacrylic acid in weight ratio in the range of about 3 to about 15 %, adjusting the pH of the solution to at least pH 5, and copolymerizing the monomeric 2-hydroxyethyl methacrylate and acrylic or methacrylic acid.

30 In addition to the uses as hydrogels, pressure sensitive adhesives, and flexible films or coatings, the poly 2-hydroxyethyl methacrylate/acrylic acid or



methacrylic acid copolymer prepared in water can also be used as an abrasion resistant coating for glass bottles. Crosslinkers and surfactants may be added to the poly 2-hydroxyethyl methacrylate/acrylic acid or methacrylic acid copolymer coatings to achieve optimum coating performance.

5

The crosslinker may be added to the copolymer in an amount from about 1 to about 10 percent by weight based on the weight of the copolymer. Suitable crosslinkers include, but are not limited to, formaldehydes, metal salts, aziridines, isocyanates, dichromates and the like. A preferred crosslinker that may be added to the copolymer is ammonium dichromate, and is added to the copolymer at about 7.5% by weight, based on the weight of the copolymer.

The surfactant may also be added to the copolymer in an amount from about 0 to about 5 percent by weight based on the weight of the copolymer. Suitable surfactants include, but are not limited to, water dispersible silicone and fluorocarbon surfactants. A preferred surfactant that may be added to the copolymer is a silicone surfactant that is commercially available from Dow Corning, and is added to the copolymer at about 2% by weight, based on the weight of the copolymer.

20

The copolymer coating can be easily removed from the glass bottles by alkali treatment, such as an alkaline solution of 1% sodium hydroxide.

In addition to its applicability to hydrophilic coatings and pressure sensitive adhesives, the present invention provides a method for the preparation of an acrylic emulsion ink jet receptive clear coating. In this embodiment, the method includes forming an alkyl acrylate monomer-containing pre-emulsion feed mixture, introducing an activator into the alkyl acrylate monomer-containing pre-emulsion feed mixture, reacting a water soluble monomer feed in the alkyl acrylate monomer-containing pre-emulsion feed mixture, wherein the weight ratio of the alkyl acrylate monomer-containing pre-emulsion feed mixture to the water soluble monomer feed

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is from about 1:1 to about 1:2, to form a clear, transparent polymer in the alkyl acrylate monomer-containing emulsion feed mixture. The alkyl acrylate monomers may include, but are not limited to, ethyl acrylate, 2-ethylhexyl acrylate, butyl acrylate, isooctyl acrylate, and the like. A preferred alkyl acrylate monomer is  
5 butyl acrylate. The water soluble monomer feed comprises 2-hydroxyethyl methacrylate and a cationic monomer, such as n-vinylpyrrolidone, wherein the weight ratio range of the 2-hydroxyethyl methacrylate to the cationic monomer is from about 1:0 to about 1:1. The term "clear" as used herein to describe the polymer refers to a polymer product that does not include particulate or inclusions  
10 that would indicate incompatibilities in the polymerization process. The term "transparent" as used herein to describe the polymer refers to a polymer product that is capable of being seen through. Both "clear" and "transparent" appearances are based upon unaided, visual inspection.

15 In one embodiment, the 2-hydroxyethyl methacrylate contains at least 0.05% by weight of ethylene glycol dimethacrylate.

The acrylic emulsion ink jet receptive clear coating of the present invention does not require the addition of fillers or particulate to obtain ink absorbency, and is  
20 particularly useful with ink jet printers that use dye based inks.

In a variation of this embodiment, the preformed clear polymer in the alkyl acrylate monomer-containing emulsion mixture is subsequently reacted with a water insoluble monomer feed mixture, for example comprising 2-hydroxyethyl  
25 methacrylate, n-vinyl pyrrolidone, butyl acrylate, and methacrylic acid, in a weight ratio of about 20% to about 80% to form a second clear polymer substantially over the preformed clear polymer in the alkyl acrylate monomer-containing emulsion mixture.

30 The addition of the water soluble monomer feed to the alkyl acrylate monomer-containing pre-emulsion feed mixture produces a first clear, or core polymer formed in the alkyl acrylate monomer-containing pre-emulsion mixture. A

second clear polymer, may be formed in the presence of the first polymer from a second monomer charge which is, in one embodiment, the water insoluble monomer feed comprising 2-hydroxyethyl methacrylate, n-vinyl pyrrolidone, butyl acrylate and methacrylic acid. The second clear polymer is formed substantially over the  
5 first clear polymer.

This polymerization process is known as sequential polymerization. It is believed that the product is a domain-type emulsion polymer in which the first or core particles form one domain and the second or shell copolymer forms a second  
10 domain which partially or continuously surrounds the core. By reserving a significant amount of the monomers to the second charge one can effectively use the monomers of the second charge to control properties.

The two systems are depicted to Figure Nos. 1 and 2. With reference to  
15 Figure 1, a sequentially polymerized polymer particle is formed in a reaction emulsion mixture as particle 10 and comprised of a central domain 12 completely or partially surrounded by a second stage polymerized outer domain 14. In their formation, the monomers of the inner domain are polymerized first, followed by polymerization of the monomers forming the outer domain which associate with and  
20 are believed to attach to the initially formed inner domain copolymer particles.

As depicted in Figure 2, if the individual polymers are separately polymerized and mixed, they form a random blend of core 16 and shell 18 polymer particles with little or no attachment or association with each other.

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As discussed above, an initiator is added to the monomeric 2-hydroxyethyl methacrylate monomers and, optionally, n-vinyl pyrrolidone, in an amount effective to initiate copolymerization. Suitable initiators include dissociative initiators and redox initiators. Suitable dissociative initiators include, but are not limited to,  
30 persulfates such as ammonium persulfate, potassium persulfate and sodium persulfate, hydrogen peroxide, tert-butyl hydroperoxide, and azo compounds such

as 4,4'-azobis(4-cyanovaleric acid). Redox initiators include, but are not limited to, persulfates with bisulfate ion, such as sodium persulfate with sodium metabisulfite, hydrogen peroxide with ferrous ion, sulfite ion, bisulfite ion or ascorbic acid, and hydroperoxides with sulfoxylates, such as tert-butyl hydroperoxide with sodium  
5 formaldehyde sulfoxylate.

A preferred activator is sodium formaldehyde sulfoxylate, preferably in an amount of about 0.1 to about 1 weight percent based on the weight of the polymer. The water insoluble monomer feed may further comprise an effective amount of an  
10 initiator, such as tert-butyl hydroperoxide or the like, and at least one water insoluble acrylate or methacrylate selected from methyl acrylate, methyl methacrylate, 2-ethylhexyl acrylate, butyl acrylate, trifluoroethyl methacrylate, and mixtures thereof in the amount of about 15 to about 35% by weight of the polymer, preferably from about 15% by weight of the polymer. Trifluoroethyl methacrylate  
15 is preferably included in the water insoluble monomer feed in an amount of about 1.5% by weight, based on the weight of the polymer. Inclusion of trifluoroethyl methacrylate results in the improvement of sheet feeding performance during inkjet printing.

20 The substrate which is used in the present invention may be any substrate material such as paper and polymeric films in the form of sheets and strips, and the like. Preferred types of paper include semi-gloss paper and high gloss paper. In one embodiment, the substrate is a polymeric film. In a preferred embodiment, the substrate is a polymeric film formed from a thermoplastic material. In a more  
25 preferred embodiment, the substrate is a polymeric film selected from the group consisting of polystyrene, a polyester, and a polyolefin such as polyethylene or polypropylene.

The acrylic emulsion ink jet receptive clear coatings of the present invention  
30 are particularly suited as coatings for clear films and high gloss photo quality paper. It is an advantage of the present invention that these acrylic emulsion ink jet

receptive coatings are clear, water resistant, have good ink absorption with quick drying, and low surface friction to enhance sheet feeding in ink jet printers. It is also an advantage of the present invention that the above properties may be achieved without the use of pigments or mixtures of polymers that would be expected to  
5 reduce the clarity of the coatings.

In another embodiment, the present invention provides a method for the preparation of a gel free hydrophilic polymer substantially in the absence of a chain transfer agent comprising a copolymer of 2-hydroxyethyl methacrylate and 4-  
10 hydroxybutyl acrylate, including introducing monomeric 2-hydroxyethyl methacrylate containing 0.05 to 0.1% by weight of ethylene glycol dimethacrylate impurities, into an alcohol solution with 4-hydroxybutyl acrylate, polymerizing the 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate to form a polymerization mixture, and removing the alcohol. The alcohol is selected from one of methanol  
15 and ethanol, with ethanol being preferred.

In another embodiment, the monomeric 2-hydroxyethyl methacrylate contains no more than about 3% by weight of alkylene glycol methacrylate impurities.

20

The copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate is a hydrophilic copolymer that is insoluble in water and does not require crosslinking for water resistance. In addition, the copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate is flexible enough to form a flexible  
25 coating or film for medical and skin care or skin protection applications without the need for the addition of glycerin. The flexible coating comprising the copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate is also useful as a rubber or latex glove coating, with particular usefulness in wet-donning applications. Rubber or latex gloves require the ability of donning, that is, the ability to slide on  
30 and off the surface of the skin with minimal friction. The copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate provides a flexible, non-

tacky glove coating that allows the donning, wet or dry, of the rubber or latex glove with minimal blocking and without undue friction or clinging.

In another embodiment, the copolymer product of 2-hydroxyethyl  
5 methacrylate and 4-hydroxybutyl acrylate may further contain up to about 10 weight percent of an additional monomer, based on the weight of the copolymeric product. More preferably, the copolymeric product may contain from about 2 to about 4 weight percent of the additional monomer. The inclusion of up to about 10 weight  
10 percent of the monomer increases the cohesive strength of the copolymer, while still maintaining pressure sensitive adhesive properties, skin coating properties, and water resistance. Useful monomers include alkyl acrylates, alkyl methacrylates, hydroxyalkyl acrylates, hydroxyalkyl methacrylates, N-vinyl lactams, vinyl acetate and styrene monomers.

15 The present invention, therefore, provides a gel-free, hydrophilic copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate that does not to be plasticized with either water or glycerin. The copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate is a water-insoluble, water-absorbing, amphilic, elastic, abrasion resistant and has improved mechanical properties.  
20 Additionally, the copolymer has a high moisture vapor transmission rate that is skin friendly and, therefore, is "skin friendly."

In another embodiment, the present invention provides a copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate is prepared substantially in  
25 the absence of a chain transfer agent. The copolymer is prepared by introducing monomeric 2-hydroxyethyl methacrylate with 4-hydroxybutyl acrylate into a solution of water and alcohol. The monomeric 2-hydroxyethyl methacrylate should contain ethylene glycol dimethacrylate impurities in the range of about 0.05 to about 0.1 % by weight. The monomers of 2-hydroxyethyl methacrylate and 4-  
30 hydroxybutyl acrylate are copolymerized to form a polymerization mixture and the alcohol/water solution is substantially removed.

The copolymerization reaction of the monomeric 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate is carried using a water-soluble initiator system. The use of a water-soluble initiator system results in a more efficient conversion of monomers into copolymer product and, therefore, reducing the amount of residual monomer remaining after the copolymerization reaction. Reducing the amount of residual monomer remaining in the polymerization mixture avoids the need of an extensive leaching process to remove the residual monomers and the remaining water-soluble initiator, which results in a time and cost savings.

In a preferred embodiment, the monomeric 2-hydroxyethyl methacrylate contains alkylene glycol impurities in the range of no more than about 3% by weight, wherein the alkylene glycol impurities are selected from ethylene glycol dimethacrylate, diethylene glycol monomethacrylate, methacrylic acid and mixtures thereof.

In general, the copolymers of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate can be utilized as a topical skin coating or barrier. Some useful applications of the copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate includes use as sprayable carriers for topical application of drugs to the skin. For this application, the copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate may be mixed with an alcohol or glycol solution to produce a sprayable vehicle or carrier that can be sprayed directly onto the skin. The copolymer may also be a component of a cream, including water in oil emulsions and oil in water emulsions, lotions, which are suspensions in water or oil, ointments, which are solutions in petroleum or polyethylene glycol, or aerosols, which are sprayable solutions in water/alcohol and gels.

The copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate may also be a component of a transdermal drug delivery system. Specifically, the water-insoluble copolymer can be used as a carrier or vehicle to deliver an effective amount of a pharmacologically active agent (drug) transdermally. In this embodiment, the copolymer may be loaded with an effective amount of a

pharmacologically active agent and locally placed on the surface of the skin. The transdermal drug delivery system can also include, as known in the art, skin permeation enhancers to facilitate the transdermal delivery of the pharmacologically active agent. The copolymer performs a dual function as a carrier of a  
5 pharmacologically active agent and a protective coating or skin barrier.

The copolymers of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate can be sprayed onto the skin before the application of adhesive-coated bandages, tapes, or other adhesive-coated medical devices to prevent irritation of sensitive  
10 skin.

The copolymers of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate can be used as an elastomeric medical film. Preferably, the copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate can be coated onto a  
15 substrate, such as a release liner and dried. The copolymer will be self cross-linking with heat treatment. Preferably, the copolymer will be self cross-linking by heat treating at a temperature in the range of about 70°C to about 150°C, more preferably in a temperature range of about 70°C to about 125°C. The elastomeric medical film can be used directly over a wound on the skin to provide a dressing or  
20 barrier. The elastomeric film is soft and pliable, and easily conforms to the contours of human skin.

The copolymers of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate can be used as a coating for gloves, such as rubber or latex medical gloves. The use  
25 of the copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate to coat a rubber or latex glove reduces the friction between the inner surface of the glove and the skin surface of the person donning the glove, especially under conditions of wet donning. The use of the copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate as a glove coating, therefore, alleviates  
30 the need for the use of powder or other lubricating materials with the gloves.



The copolymers of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate may also be included in sun block and sunscreen lotions, creams and sprays. as a carrier or vehicle of ultra-violet (UV) light absorbers, such as aminobenzoic acid, benzophenone-8 and benzophenone-4.

5

The copolymers of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate can be used as a carrier for water resistant cosmetic products. The cosmetic composition comprising the copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate is easy to apply to and remove from the surface of human  
10 skin, it is non-greasy, and non-occlusive. Like skin, the copolymers of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate are water insoluble, hydrophilic, amphiphilic, elastic and abrasion resistant.

The copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate  
15 can also be included as a component of a nasal spray or other mucus membrane drug delivery systems, as a carrier for a pharmacologically active agent, such as a pharmaceutical. Using a mucus membrane drug delivery system is a potential benefit over ingestion of pills, tablets or capsules, or repeated injections of pharmacologically active agents, because these traditional methods have initially  
20 high concentrations of the pharmacologically active agent, which may be toxic or cause side effects to the target organ or surrounding structures. As time passes, the concentration of the pharmacologically active agent diminishes and another dosage is required to maintain the pharmacologically effective level. Utilizing a mucus membrane drug delivery system including the copolymer of 2-hydroxyethyl  
25 methacrylate and 4-hydroxybutyl acrylate as a carrier for a pharmacologically active agent may permit the delivery of an effective amount of a pharmacologically active agent and maintenance of the pharmacologically effective level over longer periods of time.

30 In another embodiment, the copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate is blended with a polyalkylene glycol, such as polyethylene glycol, to form a pressure sensitive adhesive. The pressure sensitive adhesive

product can be coated onto a substrate, such as a release liner. The pressure sensitive adhesive products can be used as a bandage, tape, wound dressing, surgical drapes and ostomy site dressings.

- 5           The copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate can further be used as a lubricant for speed swimming. The copolymer may be applied to the skin of a swimmer, for example prior to competitive swimming events. As described above, the copolymer may be applied to the skin of a swimmer by spraying the copolymer directly onto the skin.

10

- In another embodiment, the copolymer product of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate, prepared in a solution of water and alcohol, may further contain up to about 10 weight percent of an additional monomer, based on the weight of the copolymeric product. More preferably, the  
15 copolymeric product may contain from about 2 to about 4 weight percent of the monomer. The inclusion of up to about 10 weight percent of the monomer increases the cohesive strength of the copolymer, while still maintaining pressure sensitive adhesive properties, skin coating properties, and water resistance. Useful monomers include alkyl acrylates, alkyl methacrylates, hydroxyalkyl acrylates,  
20 hydroxyalkyl methacrylates, N-vinyl lactams, vinyl acetate and styrene monomers.

- In another embodiment, the present invention provides a method for the preparation of a powdered low-gel poly 2-hydroxyethyl methacrylate substantially in the absence of a chain transfer agent is also provided comprising: introducing  
25 monomeric 2-hydroxyethyl methacrylate containing ethylene glycol dimethacrylate impurities in the range of 0.05 to 0.1% by weight into water, polymerizing the 2-hydroxyethyl methacrylate, drying said polymerized 2-hydroxyethyl methacrylate, and grinding said dried polymerized 2-hydroxyethyl methacrylate to form a powder.

In another embodiment, the monomeric 2-hydroxyethyl methacrylate contains alkylene glycol methacrylate impurities in the range of no more than 3% by weight.

5 In a variation of this embodiment, the method for the preparation of a low-gel poly 2-hydroxyethyl methacrylate substantially in the absence of a chain transfer agent, comprises introducing monomeric 2-hydroxyethyl methacrylate containing ethylene glycol dimethacrylate impurities in the range of no more than about 0.05 to 0.1% by weight into water, polymerizing the 2-hydroxyethyl methacrylate to form a  
10 polymerization mixture, drying the polymerized 2-hydroxyethyl methacrylate, and grinding the dried polymerized 2-hydroxyethyl methacrylate to form a powder. The dry poly 2-hydroxyethyl methacrylate powder is then blended with a polyalkylene glycol, such as polyethylene glycol, to form a pressure sensitive adhesive, wherein the amount of the polyalkylene glycol used to prepare the pressure sensitive  
15 adhesive is from about 40 to about 70% by weight, based on the weight of the dry poly 2-hydroxyethyl methacrylate powder and the polyethylene glycol.

In another embodiment, the 2-hydroxyethyl methacrylate monomer contains alkylene glycol impurities that are selected from the group consisting of ethylene  
20 glycol dimethacrylate, diethylene glycol monomethacrylate, methacrylic acid and mixtures thereof, in a total amount of no more than about 3% by weight of monomer.

The hydrophilic pressure sensitive adhesive formed by this method has utility  
25 in many label and tape applications, and is particularly suitable for thick medical applications, and as an additive for cosmetic and skin care products. In another variation of this embodiment, the dry poly 2-hydroxyethyl methacrylate powder can be dissolved in alcohol and glycerin can be added to the polymerization mixture in an amount from about 10% to about 50% by weight of the polymer, preferably  
30 about 25% by weight of the polymer, and the alcohol removed to form a flexible

hydrophilic coating. Before, the alcohol is removed, the solution can be sprayed onto the skin prior to applying a bandage, glove, or the like.

5 In another embodiment, the present invention provides a method for the preparation of a gel free hydrophilic homopolymer of 4-hydroxybutyl acrylate substantially in the absence of a chain transfer agent. The method includes introducing monomeric 4-hydroxybutyl acrylate into a solution of water and alcohol, and polymerizing the 4-hydroxybutyl acrylate. As described above, the alcohol is selected from one of methanol and ethanol, with ethanol being preferred.

10

In another embodiment, the invention also provides a method for the preparation of a gel-free homopolymer of 4-hydroxybutyl acrylate in alcohol and substantially in the absence of a chain transfer agent comprising. The monomeric 4-hydroxybutyl acrylate is introduced into an alcohol solution. The monomeric 4-  
15 hydroxybutyl acrylate is polymerized to form a polymerization mixture.

In another embodiment, the invention provides substrates coated with the homopolymer of 4-hydroxybutyl acrylate prepared in a solution of water and alcohol and a method of coating a substrate comprising applying to the substrate the  
20 polymerization mixture of a homopolymer of 4-hydroxybutyl acrylate prepared in a solution of water and alcohol and, thereafter, removing the alcohol and water from the polymerization mixture. In a preferred embodiment, the substrate is a release liner.

25 In another embodiment, the invention provides a method of coating a substrate comprising applying to the substrate the polymerization mixture of a homopolymer of 4-hydroxybutyl acrylate prepared in a solution of water and alcohol, and further comprising adding a polyalkylene glycol to the polymerization mixture prior to the removing of the alcohol and water, and thereafter removing the alcohol  
30 from the polymerization mixture to form a hydrophilic pressure sensitive adhesive upon removing the alcohol and water from the polymerization mixture. The

polyalkylene glycol to be added to the polymerization mixture containing the homopolymer of 4-hydroxybutyl acrylate may be selected from, but should not be limited to, polyethylene glycol, polypropylene glycol, copolymers of ethylene glycol and propylene glycol and mixtures thereof.

5

It should be noted, however, that the homopolymer of 4-hydroxybutyl acrylate may form a hydrophilic pressure sensitive adhesive even without the addition of a polyalkylene glycol to the polymerization mixture. However, the addition of a polyalkylene glycol to the polymerization mixture prior to removing the solution of alcohol and water may enhance the adhesive properties of the resulting pressure sensitive adhesive.

The homopolymer of 4-hydroxybutyl acrylate prepared in a solution of water and alcohol, like the copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate, has a wide variety of applications. As described above for the copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate, the homopolymer of 4-hydroxybutyl acrylate can be used to prepare elastomeric films for medical applications.

The homopolymer of 4-hydroxybutyl acrylate may also be used as a carrier for a transdermal drug delivery system or a mucus membrane drug delivery system. The carrier may be loaded with a pharmacologically active agent, such as a pharmaceutical.

The homopolymer of 4-hydroxybutyl acrylate is also useful for the preparation of creams, lotions, and ointments.

The homopolymer of 4-hydroxybutyl acrylate may also be used to prepare aerosol and spray compositions for direct application to the skin.

30

The homopolymer of 4-hydroxybutyl acrylate may also be used to prepare a skin friendly cosmetic composition.

5 The homopolymer of 4-hydroxybutyl acrylate may also be used to prepare a coating comprising the homopolymer. The coating compositions find particular application in the coating of rubber or latex gloves, such as the surgical gloves used in the medical field.

10 In another embodiment, the homopolymer product of 4-hydroxybutyl acrylate may further contain up to about 10 weight percent of an additional monomer, based on the weight of the polymeric product. More preferably, the polymeric product may contain from about 2 to about 4 weight percent of the monomer. The inclusion of up to about 10 weight percent of the monomer increases the cohesive strength of the homopolymer, while still maintaining pressure sensitive  
15 adhesive properties, skin coating properties, and water resistance. Useful monomers include alkyl acrylates, alkyl methacrylates, hydroxyalkyl acrylates, hydroxyalkyl methacrylates, N-vinyl lactams, vinyl acetate and styrene monomers.

In another embodiment, the present invention provides a method for the  
20 preparation of a gel free hydrophilic homopolymer of 2-hydroxyethyl methacrylate substantially in the absence of a chain transfer agent. The method includes introducing monomeric 2-hydroxyethyl methacrylate containing no more than about 0.05-0.1% by weight of ethylene glycol dimethacrylate into a solution of water and alcohol, and polymerizing the 2-hydroxyethyl methacrylate.

25

In a variation of this method, the monomeric 2-hydroxyethyl methacrylate contains no more than about 3% by weight alkylene glycol methacrylate impurities. Preferably, the alkylene glycol methacrylate impurities are selected from, but are not limited to, ethylene glycol dimethacrylate, diethylene glycol monomethacrylate,  
30 methacrylic acid and mixtures thereof. Again, the alcohol used in the water/alcohol mixture and into which the monomeric 2-hydroxyethyl methacrylate is introduced

includes, but should not be limited to, methanol and ethanol, with ethanol being preferred.

The invention also provides a substrates coated with the homopolymer of 2-hydroxyethyl methacrylate prepared in a solution of water and an alcohol and a method of coating a substrate comprising applying to a substrate a polymerization mixture containing the homopolymer of 2-hydroxyethyl methacrylate and, thereafter, removing the alcohol and water from the polymerization mixture. In one preferred embodiment, the substrate is a release liner.

10

In another embodiment, the invention provides hydrophilic pressure sensitive adhesives prepared by adding a polyalkylene glycol to the homopolymer of 2-hydroxyethyl methacrylate prepared in a solution of water and alcohol, and a method of coating a substrate comprising applying to a substrate a polymerization mixture containing the homopolymer of 2-hydroxyethyl methacrylate, and further comprising adding a polyalkylene glycol to the polymerization mixture prior to the removing of the alcohol and water, to form a hydrophilic pressure sensitive adhesive upon removing said alcohol and water. In one preferred embodiment, the substrate is a release liner. The polyalkylene glycol that is added to the polymerization mixture containing the homopolymer of 2-hydroxyethyl methacrylate may be selected from, but is not limited to, polyethylene glycol, polypropylene glycol, copolymers of ethylene glycol and propylene glycol and mixtures thereof.

20

The homopolymer of 2-hydroxyethyl methacrylate prepared in a solution of water and alcohol, like the homopolymer of 4-hydroxybutyl acrylate, has a wide variety of applications. As described above for the homopolymers of 4-hydroxybutyl acrylate, the homopolymer of 2-hydroxyethyl methacrylate can be used to prepare elastomeric films for medical applications.

25

The homopolymer of 2-hydroxyethyl methacrylate may also be used as a carrier for a transdermal drug delivery system or a mucus membrane drug delivery

30

system. The carrier may be loaded with a pharmacologically active agent, such as a pharmaceutical.

5 The homopolymer of 2-hydroxyethyl methacrylate is also useful for the preparation of creams, lotions, and ointments.

The homopolymer of 2-hydroxyethyl methacrylate may also be used to prepare aerosol and spray compositions for direct application to the skin.

10 The homopolymer of 2-hydroxyethyl methacrylate may also be used to prepare a skin friendly cosmetic composition.

15 The homopolymer of 2-hydroxyethyl methacrylate may also be used to prepare a coating comprising the homopolymer. The coating compositions find particular application in the coating of rubber or latex gloves, such as the surgical gloves used in the medical field.

20 In another embodiment, the homopolymer product of 2-hydroxyethyl methacrylate may further contain up to about 10 weight percent of an additional monomer, based on the weight of the copolymeric product. More preferably, the polymeric product may contain from about 2 to about 4 weight percent of the monomer. The inclusion of up to about 10 weight percent of the monomer increases the cohesive strength of the polymer, while still maintaining pressure sensitive adhesive properties, skin coating properties, and water resistance. Useful  
25 monomers include alkyl acrylates, alkyl methacrylates, hydroxyalkyl acrylates, hydroxyalkyl methacrylates, N-vinyl lactams, vinyl acetate and styrene monomers.

30 In another embodiment, the invention also provides a method for the preparation of a gel-free homopolymer of 4-hydroxybutyl acrylate substantially in the absence of a chain transfer agent comprising introducing monomeric 4-hydroxybutyl acrylate into alcohol, and polymerizing the 4-hydroxybutyl acrylate to



form a polymerization mixture. The alcohol may be selected, without limitation, methanol and ethanol.

2-Hydroxyethyl methacrylate monomer suitable for use in the method of the present invention may also be made by blending industrial grade 2-hydroxyethyl methacrylate monomer from various sources to provide the desired level of impurities. Although less economical, 2-hydroxyethyl methacrylate monomer suitable for use in the method of the present invention may also be made by adding specified amounts of impurities to a higher purity 2-hydroxyethyl methacrylate monomer, to control the properties desired.

The polymers and copolymers of the present invention may be applied to various substrates as described below by any conventional means known in the art such as die coating, roll coating, reverse roll coating, gravure coating, reverse gravure coating, offset gravure coating, Mayer rod or wire wound rod coating, spraying, brushing, and the like. The polymers and copolymers of the present invention may be heated or cooled to facilitate the coating process and to alter the depth or penetration into the substrate.

The amount of the polymers and copolymers of the present invention applied to a substrate may be varied depending upon the characteristics of the substrate, the characteristics desired to be imparted to the substrate, and the particular characteristics of the polymers and copolymers. For economic reasons, it is normally desired to apply the lowest amount of coating to obtain the desired result. Typically, the applied coating weights may, depending on the substrate and intended use, range from about 0.1 to about 100 grams/meter<sup>2</sup>. For pressure sensitive adhesive applications, the amount is preferably in the range of about 15 grams/meter<sup>2</sup> to about 45 grams/meter<sup>2</sup>. For hydrophilic coating and ink jet coating applications, the amount is preferably from about 1 gram/meter<sup>2</sup> to about 25 grams/meter<sup>2</sup>.

Composites of the present invention may be prepared in various forms including webs which may be in roll form and which can thereafter be cut or slit into strips or sheets of desired dimensions.

5           As described hereinabove, all of the homopolymers and copolymers prepared in accordance with the methods of the present invention have a high MVTR, are water-insoluble, are flexible, hydrophilic, are water-absorbing, and have good mechanical properties.

10           All of the homopolymers and copolymers prepared in accordance with the methods of the present invention are suitable for the preparation of and use as elastomeric films, pressure sensitive adhesives, coatings, hydrogels, compositions for topical applications to the skin such as, creams, lotions, ointments, gels, aerosols, sprays, cosmetic compositions, deodorants, and insect repellants.

15           The unique combination of characteristics makes the homopolymers and copolymer suitable as medical elastomeric films, bandages, tapes, wound care dressings, surgical drapes, ostomy site dressings, as a carrier for transdermal drug delivery systems, and as a carrier for mucus membrane drug delivery systems.

20           Typical pharmacologically active agents include, but are not limited to, corticosteroids, anti-acne agents such as retinoic acid and benzoyl peroxide, anti-infectives such as erythromycin, tetracycline, and clindamycin, anti-fungals such as tolnaftate, undecylenic acid, nystatin, clotrimazole, and fluconazole, antioxidants such as butylated hydroxytoluene, t-butylhydroquinone, tocopherol, surfactants such  
25           as sodium lauryl sulfate, UV absorbers such as aminobenzoic acid, benzphenon-8, and benzophenone-4, humectants such as propylene glycol, glycerin, polyethylene glycol, and butylene glycol, alpha hydroxy acids, and emollients such as castor oil, mineral oil, petroleum cetyl palmitate, cetyl alcohol, and stearyl alcohol.

The homopolymers and copolymers prepared in accordance with the methods of the present invention are also useful as a protective coating for skin prior to the application of bandages, tapes or medical devices to the skin.

5           The following examples illustrate the method of preparation of the hydrophilic homopolymers and copolymers of the present invention. In the following examples, Disponil FES-77 is alkylpolyglycol ether sulfate, sodium salt, available from Henkel Corp., of Ambler, PA. Airvol 523 is polyvinyl alcohol, available from It should be noted that the examples are intended for illustrative  
10           purposes only, and are not intended to limit the scope of the invention in any manner.

          The presence of any gel in the polymeric product can be determined by pouring a thin film of the polymeric product and visually inspecting for any  
15           particulate in the thin polymeric film.

          The term "gel free" as used in the specification refers to a polymeric product having no particulates on visual inspection of a poured thin film of the polymeric product. The term "% insoluble" of the homopolymers and copolymers prepared  
20           according to the methods of the present invention refers to a measure of the polymer product that is insoluble in methanol (MeOH). The % insoluble of the product may be determined as follows: The polymer product is coated onto a silicone release liner and dried at 70°C for 15 minutes. The adhesive is removed from the release liner, and a 60 to 80 mg sample of the adhesive is accurately weighed out and  
25           placed into a 10 µm PTFE membrane filter. The edges of the filter are thermally sealed to contain the sample, and the filter is placed in a vial containing about 15g of methanol. The vial is agitated for 72 hours, and the filter is taken out of the solvent and dried at 120°C for 120 minutes. The filter is then weighed, and the resulting weight of the sample is used to calculate the % insoluble as follows:

30

$$\% \text{ insoluble} = (b/a) \times 100$$

wherein,

a = initial weight of the sample, and

b = final weight of the sample.

5

### EXAMPLE 1

Preparation of poly 2-Hydroxyethyl Methacrylate in Ethanol

Recipe (1807 gram batch)

#### Reactor Charge

10	2-Hydroxyethyl Methacrylate (Mitsubishi)	540 grams
	Ethanol	1080 grams
	Benzoyl peroxide	2.7 grams

#### Cook-Off initiator #1

15	Ethanol	60 grams
	2,2'-azobis(2,4-dimethylpentanenitrile)*	1.4 grams

#### Cook-Off initiator #2

	Ethanol	60 grams
20	2,2'-azobis(2,4-dimethylpentanenitrile)*	1.4 grams

#### Cook-Off initiator #3

	Ethanol	60 grams
	2,2'-azobis(2,4-dimethylpentanenitrile)*	1.4 grams

25

\* VAZO®52 (2,2'-azobis(2,4-dimethylpentanenitrile) (Dupont; Wilmington, Delaware)

PROCEDURE

1. The Reactor Charge was weighed out into a flask and poured into a reaction kettle with mixing, and was heated with an 80°C jacket and a N<sub>2</sub> purge kettle.  
5
2. The Cook-Off initiator #1 (Ethanol and VAZO®52) was weighed into a small beaker and mixed until the solids dissolved.
3. Three and one-half hours after the addition of the Reactor Charge, Cook-Off  
10 initiator #1 was added to the kettle.
4. The Cook-Off initiator #2 (Ethanol and VAZO®52) was weighed into a small beaker and mixed until the solids dissolved.
- 15 5. One hour after the addition of Cook-Off initiator #1, Cook-Off initiator #2 was added to the kettle.
6. The Cook-Off initiator #3 (Ethanol and VAZO®52) was weighed into a small beaker and mixed until the solids dissolved.  
20
7. One hour after the addition of Cook-Off initiator #2, Cook-Off initiator #3 was added to the kettle.
8. One hour after the addition of Cook-Off initiator #3, the kettle contents were  
25 cooled and discharged.

The polymeric product synthesized in Example No. 1, above, exhibited the following properties:

- Appearance: clear to light-yellow gel-free liquid  
30 Solids: 30.5 %  
Viscosity: 8,700 cPs

Residual monomer: HEMA, 0.95%

Molecular weight: 483K, PD 6.1

5 The appearance of the polymeric product in this example was determined utilizing a visual test looking at the clarity and color of the polymeric product. The presence of any gel in the polymeric product was determined by pouring a thin film of the product and visually inspecting for any particulate.

10 The percent solids in the polymeric product was measured by accurately weighing a small aluminum dish, then accurately weighing about 1 gram of wet polymer sample. The aluminum dish with the sample was dried under an infrared lamp for about 15 minutes. The aluminum dish with the dried sample was cooled and then accurately reweighed. The weight of the dried sample divided by the wet sample multiplied by 100 is the percent total solids in the sample.

15

The viscosity of the polymeric product was measured under ambient conditions (23-25°C) with a Brookfield LV Viscometer using an appropriate spindle and speed for the measured viscosity. The viscosity units are centipoise, cPs.

20 The molecular weight of the polymeric product was measured using Gel Permeation Chromatography (GPC) in methanol with polyethylene glycol standards.

25 The protocols described hereinabove that were used to measure and evaluate the appearance, percent solids, viscosity and molecular weight of the polymeric product of Example No. 1 apply to all of the representative homopolymer and copolymer products produced according to the present invention, unless specifically indicated.

30 Example Nos. 2-6 are representative poly 2-hydroxyethyl methacrylates prepared in ethanol according to the present invention with 2-hydroxyethyl methacrylate monomers having alkylene glycol methacrylate impurities less than

3%, and wherein the alkylene glycol methacrylate impurities comprise ethylene glycol dimethacrylate impurities are between 0.05 and 0.1% by weight, and are compared to Comparative Example Nos. 7 and 8, which are poly 2-hydroxyethyl methacrylates prepared with 2-hydroxyethyl methacrylate monomers having  
 5 alkylene glycol methacrylate impurities less than 3% and with ethylene glycol dimethacrylate greater than 0.15%. As Table I shows, substantially gel-free hydrophilic poly 2-hydroxyethyl methacrylates can be synthesized in ethanol. The poly 2-hydroxyethyl methacrylates can achieve molecular weights, Mw (weight  
 10 average molecular weight), from about 176,000 to about 1,000,000, molecular weights, Mn (number average molecular weight), from about 59,000 to about 250,000, solids contents of about 30 weight percent, and a viscosity of about 1000 to about 100,000 cPs.

15

TABLE I  
 Synthesis of Poly 2-hydroxyethyl methacrylate in Ethanol

Example No.	2	3	4	5	6	C7	C8
HEMA used <sup>a</sup>	Mitsubishi	Mitsubishi	Mitsubishi	Mitsubishi	Mitsubishi	Rohm & Haas	Rohm & Haas
Initiator	AIBN <sup>b</sup> , 0.5%	BPO <sup>c</sup> , 0.5%	BPO, 0.5%	BPO, 0.5%	BPO, 0.25%	AIBN, 0.5%	AIBN, 0.5%
Solids Content, %	30	30.9	30.5	30.7	31.3	gelled	gelled
Viscosity, cPs	1090	7100	8700	15150	82,000	----	----
Mol. wt, Mw	176,000	420,000	483,000	874,000	1,070,000	----	----
Mol. wt, Mn	59,200	68,000	78,700	187,000	252,000	----	----

a-source of 2-hydroxyethyl methacrylate monomer

b-AIBN (azobisisobutyronitrile)

c-BPO(Benzoyl Peroxide)

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Table I shows that the preparation of poly 2-hydroxyethyl methacrylate (poly HEMA) polymers, substantially in the absence of chain transfer agents, using the Mitsubishi HEMA monomer source having acceptable impurity levels provides high molecular weight gel free poly HEMA solution in alcohol. The molecular weight of  
 25 the polymers can be varied by adjusting the type and amount of initiator used. The use of the AIBN initiator provides the lowest molecular weight polymer. In contrast, the poly HEMA prepared with Rohm & Haas HEMA monomer having 0.17% ethylene glycol dimethacrylate impurity levels, provided a gelled poly HEMA in alcohol, even when using AIBN as the initiator.

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## EXAMPLE 9

## Preparation of poly 2-Hydroxyethyl Methacrylate in Methanol

## Recipe (982 gram batch)

Reactor Charge

5	2-Hydroxyethyl Methacrylate (Mitsubishi)	300 grams
	Methanol	700 grams
	AIBN (2,2'-azobis(isobutyronitrile))	1.5 grams

Cook-Off initiator

10	Methanol	15 grams
	AIBN (2,2'-azobis(isobutyronitrile))	0.75 grams

PROCEDURE

- 15 1. The Reactor Charge was weighed out into a flask and poured into a reaction kettle with mixing, and was heated with an 65°C jacket and a N<sub>2</sub> purge kettle.
2. The Cook-Off initiator (Methanol and AIBN) was weighed into a small beaker and mixed until the solids dissolved.
- 20 3. Six hours after adding the Reactor Charge the Cook-Off initiator was added.
4. Four hours after adding the Cook Off initiator, the kettle contents were cooled and discharged.

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The polymeric product synthesized in Example No. 9, above, exhibited the following properties:

Appearance: clear to light-yellow gel-free liquid

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Solids: 36.7%

Viscosity: 39,000 cPs



Residual monomer: HEMA, 0.78%

Molecular weight: Mw=2,260K, PD 4

The shear (min) and 180° peel adhesion properties of pressure sensitive adhesives prepared according to the present invention was evaluated. Table II, below, shows the shear properties and peel adhesion properties of pressure sensitive adhesives on substrates, such as stainless steel, high density polyethylene, and recycled cardboard. As Table II shows, pressure sensitive adhesives prepared by blending poly 2-hydroxyethyl methacrylate synthesized in methanol with 2-hydroxyethyl methacrylate monomers having alkylene glycol methacrylate impurities less than 3% by weight and with ethylene glycol dimethacrylate less than 0.1% and polyethylene glycol (PEG) have a 180° peel adhesion after twenty minutes of about 0.75 lb/in to about 4 lb/in on a stainless steel substrate, a 180° peel adhesion of about 0.2 lb/in to about 0.4 lb/in on a high density polyethylene substrate, and a 180° peel adhesion of about 1 lb/in to about 2 lb/in on a recycled cardboard substrate.

Table II also shows that pressure sensitive adhesives prepared by blending poly 2-hydroxyethyl methacrylate prepared with 2-hydroxyethyl methacrylate monomers having alkylene glycol methacrylate impurities less than 3% by weight and with ethylene glycol dimethacrylate impurity less than 0.1% with polyethylene glycol has a 180° peel adhesion after 24 hours of about 2.3 lb/in to about 4.3 lb/in on a stainless steel substrate, a 180° peel adhesion of about 0.3 lb/in to about 1 lb/in on a high density polyethylene substrate, and a 180° peel adhesion of about 2 lb/in to about 3.7 lb/in on a recycled cardboard substrate.

**TABLE II**  
**Poly 2-Hydroxyethyl Methacrylate synthesized in Methanol**  
**and Pressure Sensitive Adhesives**

Example No.	Resin/PEG	Coat Weight g/m <sup>2</sup>	Shear, min ¼ in <sup>2</sup> , 500g	180° Peel, lb/in 20', SS	180° Peel, lb/in 20', HDPE	180° Peel, lb/in 20' RC	180° Peel, lb/in 24h, SS	180° Peel, lb/in 24h, HDPE	180° Peel, lb/in 24h RC
10	1:1	38.1	2 c	0.75 p	0.2 p	2.0 sl. c	2.3 p	0.3 p	3.6 c
11	1.2:0.8	33.6	98 c	4.0 pt	0.4 p	1.7 sl. pt	4.2 pt	1.0 p	3.7 pt
12	1.3:0.7	30.7	143 c	3.5 pt	0.3 p	1.1 sl. pt	4.3 pt	0.6 p	2.0 pt

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SS - stainless steel; HDPE - high density polyethylene; RC - recycled cardboard  
 c - cohesive; p - panel; pt - paper tear; sl. - slight

Table II shows that polyHEMA polymers prepared in alcohol can be formulated with a plasticizer, such as polyethylene glycol (PEG) 400 (Carbowax; Union Carbide) to provide a pressure sensitive adhesive. The adhesive performance of the pressure sensitive adhesive can be varied by adjusting the amount of polyethylene glycol used in the preparation. A polyHEMA:PEG ratio in the range of about 1.5:0.5 to about 0.5:1.5 is used to prepare the pressure sensitive adhesive. Preferably, a polyHEMA:PEG ratio of about 1.2:0.8 is used to prepare the pressure sensitive adhesive.

Static shear measures the time required to remove a test sample from a substrate under a specific load. The test applies to the static force to remove an affixed pressure sensitive adhesive from a standard flat surface when the load acts parallel to the surface in a pure shearing action. In static shear testing, the samples were cut into 12 x 51 mm test strips. The test strips were applied to brightly annealed, highly polished stainless steel test panels having a typical size of about 50 x 75 mm, making a sample overlay of 12 x 12 mm with the test panel. The sample portion on the test panel was rolled on using a 2 kg, 5.45 pli 65 shore "A" rubber-faced roller, rolling back and forth one at a rate of 30 cm/min. After a dwell time of at least 15 minutes under standard laboratory testing conditions, the test panels with the test strips were placed at a 2° angle from the vertical, and a load of 500g

was attached to the end of the test strips. The time (in minutes) for the test sample to fail cohesively was measured by a timer.

To measure the peel adhesion, the adhesive was coated at an approximate  
5 coat weight of 25 g/m<sup>2</sup> (1.0 mil) onto a silicone coated release liner, and then laminated to a 2 mil Mylar™ facestock to form a laminate construction. The resulting laminate was die-cut into 25 x 204 mm sized test strips. The test strips were then applied to 50 x 152 mm brightly annealed, highly polishes stainless steel test panels in the lengthwise direction, and rolled down using a 2 kg 5.45 pli 65  
10 shore "A" rubber faced roller. The roller was rolled back and forth once over the test strip at a rate of 30 cm/min. The samples were conditioned for either 15 minutes or 24 hours in a controlled environment testing room maintained at 20°C and 50% relative humidity. After conditioning, the test strips were peeled away from the test panel in an Instron Universal Tester according to a modified version of  
15 the standard tape method Pressure-Sensitive Tape Council, PSTC-1. The force to remove the adhesive test strips from the test panel was measured in lbs/in. Glass panels and high density polyethylene panels were also used to measure peel adhesion.

20 Possible adhesion failure modes were: "panel failure," wherein the adhesive construction detached from the panel cleanly, without leaving any residue; "panel staining," wherein the adhesive construction detached cleanly, but left a faint stain or "shadow" on the panel; "cohesive failure," wherein the adhesive construction split apart, leaving residue on the test panel and the facestock; "facestock failure,"  
25 wherein the adhesive completely detached from the facestock, and transferred to the test panel; and "mixed," wherein mixed failure modes were evident.

## EXAMPLE 13

Preparation of HEMA/Methacrylic Acid Copolymer in Water  
Recipe (1200g batch)5    Reactor Charge

Deionized Water	400.00 g
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Initiator Charge

Deionized Water	100.00 g
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Sodium Persulfate	1.5 g
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10   Monomer Feed

2-Hydroxyethyl Methacrylate	270.0 g
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Methacrylic Acid	30.00 g
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Deionized Water	300.00 g
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Ammonium Hydroxide (30%)	12.3 g
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15   Cook-Off Initiator #1

Deionized Water	50.0 g
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Sodium Persulfate	0.75 g
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Cook-Off Initiator #2

Deionized Water	50.0 g
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20   Sodium Persulfate	0.75 g
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PROCEDURE

1.    The Reactor Charge was weighed out into a flask and poured into a reaction kettle.
- 25   2.    The Reactor Charge was heated with an 80°C jacket and a N<sub>2</sub> purge kettle.
3.    The Monomer Feed (2-hydroxyethyl methacrylate, methacrylic acid, deionized water) was weighed into a feed jar, then ammonium hydroxide was
- 30   added with mixing to adjust the pH to about 5.5.

4. The Initiator Charge (sodium persulfate and deionized water) was weighed out into a small beaker and mixed until the solid dissolved.
5. The Initiator Charge was poured into the reaction kettle with the heated and N<sub>2</sub>- purged Reactor Charge.
6. After 10 minutes, the Monomer Feed was started for a 3-hour period (3.34 g/min), while maintaining an 80°C jacket temperature.
- 10 7. The Cook-Off Initiator #1 (sodium persulfate and deionized water) was weighed into a small beaker and mixed until the solid dissolved.
8. One hour after the end of the Monomer Feed, the Cook-Off Initiator #1 was poured into the reaction kettle.
- 15 9. Cook-Off Initiator #2 (sodium persulfate and deionized water) was weighed into a small beaker and mixed until the solid dissolved.
10. One hour after adding Cook-Off #1, Cook-Off #2 was added.
- 20 11. One hour after adding Cook-Off #2, the kettle contents were cooled, then discharged into a quart jar.

The copolymer product synthesized in Example No. 13, above, exhibited the following properties:

Appearance: clear, light yellow gel-free liquid.

Solids: 25.9%

Viscosity: 33,000 cPs

30 pH: 5.5

Residual monomer: HEMA <0.02%, MAA 0.09%

Molecular weight: MW 392K; polydispersity, the Mw/Mn (PD) 1.7

#### EXAMPLE 14

##### Preparation of HEMA/4-HBA Copolymer in Alcohol

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##### Recipe (1003.75g batch)

###### Reactor Charge

	2-Hydroxyethyl Methacrylate (Mitsubishi)	150 g
10	4-Hydroxybutyl Acrylate (4-HBA)	150 g
	Ethanol	600 g
	Benzoyl Peroxide	1.5 g

###### Cook-Off Initiator #1

15	Ethanol	33.3 g
	AIBN (2,2'-azobis[isobutyronitrile])	0.75 g

###### Cook-Off Initiator #2

	Ethanol	33.3 g
20	AIBN (2,2'-azobis[isobutyronitrile])	0.75 g

###### Cook-Off Initiator #3

	Ethanol	33.3 g
	AIBN (2,2'-azobis[isobutyronitrile])	0.75 g

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##### PROCEDURE

1. The Reactor Charge was weighed out into a flask and poured into a reaction kettle with mixing, heated with a 80°C jacket, and N<sub>2</sub> purged.
- 30 2. The Cook-Off Initiator #1 (Ethanol and AIBN) was weighed into a small beaker and mixed until the solids dissolved.

3. Three and one-half hours after adding the Reactor Charge, the Cook-Off Initiator #1 was poured into the reaction kettle.
4. Cook-Off Initiator #2 (Ethanol and AIBN) was weighed into a small beaker  
5 and mixed until the solids dissolved.
5. One hour after adding Cook-Off #1, Cook-Off #2 was added.
6. Cook-Off Initiator #3 (Ethanol and AIBN) was weighed into a small beaker  
10 and mixed until the solids dissolved.
7. One hour after adding Cook-Off #2, Cook-Off #3 was added.
8. One hour after adding Cook-Off #3, the kettle contents were cooled, then  
15 discharged into a quart jar.

The copolymer product synthesized in Example No. 14, above, exhibited the following properties:

- 20 Appearance: clear, light yellow gel-free liquid.  
Solids: 30.5%  
Viscosity: 844 cPs  
Residual monomer: HEMA <0.01 %, 4-HBA 0.22 %  
Glass Transition Temperature,  $T_g$ , 9°C
- 25 % Gel in water: 98%  
The copolymer is swellable in water up to twice its weight.

Table III, below, shows the static shear and peel adhesion properties of pressure sensitive adhesives prepared by blending copolymers of poly 2-hydroxyethyl methacrylate and methacrylic acid (HEMA/MAA) with a polyalkylene glycol, such as polyethylene glycol (PEG). Example Nos. 13a and 13b are pressure  
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sensitive adhesives prepared from blending HEMA/MAA copolymers and PEG. The HEMA polymers used in Example Nos. 13a and 13b were synthesized in water. Example No. 15 is a pressure sensitive adhesive prepared from blending HEMA/MAA copolymers and PEG. The HEMA/MAA copolymer used in  
5 Example No. 15 was synthesized in methanol. The HEMA polymer used in Example No. 16 was synthesized in methanol.

Static shear measures the time required to remove a test sample from a substrate under a specific load. The test applies to the static force to remove an  
10 affixed pressure sensitive adhesive from a standard flat surface when the load acts parallel to the surface in a pure shearing action. In static shear testing, the samples were cut into 12 x 51 mm test strips. The test strips were applied to brightly annealed, highly polished stainless steel test panels having a typical size of about 50 x 75 mm, making a sample overlay of 12 x 12 mm with the test panel. The sample  
15 portion on the test panel was rolled on using a 2 kg, 5.45 pli 65 shore "A" rubber-faced roller, rolling back and forth one at a rate of 30 cm/min. After a dwell time of at least 15 minutes under standard laboratory testing conditions, the test panels with the test strips were placed at a 2° angle from the vertical, and a load of 500g was attached to the end of the test strips. The time (in minutes) for the test sample  
20 to fail cohesively was measured by a timer.

To measure the peel adhesion, the adhesive was coated at an approximate coat weight of 25 g/m<sup>2</sup> (1.0 mil) onto a silicone coated release liner, and then laminated to a 2 mil Mylar™ facestock to form a laminate construction. The  
25 resulting laminate was die-cut into 25 x 204 mm sized test strips. The test strips were then applied to 50 x 152 mm brightly annealed, highly polishes stainless steel test panels in the lengthwise direction, and rolled down using a 2 kg 5.45 pli 65 shore "A" rubber faced roller. The roller was rolled back and forth once over the test strip at a rate of 30 cm/min. The samples were conditioned for either 15  
30 minutes or 24 hours in a controlled environment testing room maintained at 20°C and 50% relative humidity. After conditioning, the test strips were peeled away



from the test panel in an Instron Universal Tester according to a modified version of the standard tape method Pressure-Sensitive Tape Council, PSTC-1. The force to remove the adhesive test strips from the test panel was measured in lbs/in. Glass panels and high density polyethylene panels were also used to measure peel  
5 adhesion.

Possible adhesion failure modes were: "panel failure", wherein the adhesive construction detached from the panel cleanly, without leaving any residue; "panel staining", wherein the adhesive construction detached cleanly, but left a faint stain  
10 or "shadow" on the panel; "cohesive failure", wherein the adhesive construction split apart, leaving residue on the test panel and the facestock; "facestock failure", wherein the adhesive completely detached from the facestock, and transferred to the test panel; and "mixed", wherein mixed failure modes were evident.

As Table III shows, pressure sensitive adhesives prepared with the HEMA/MAA copolymers of the present invention, exhibit a static shear of about 16  
15 to about 170 minutes. Pressure sensitive adhesives prepared with the HEMA/MAA copolymers of the present invention exhibit a 180° peel adhesion on a stainless steel substrate of about 1.7 lb/in to about 3.4 lb/in after twenty minutes, and a 180° peel  
20 adhesion on a stainless steel substrate of about 2.7 lb/in to about 4 lb/in after 24 hours.

TABLE III

Pressure sensitive adhesives (PSA) prepared with copolymers of 2-  
25 hydroxyethylmethacrylate and methacrylic acid

Example No.	Composition	Polymer:PEG	Shear, Min	180° Peel, SS	
	HEMA/MAA	1:1	¼ in <sup>2</sup> , 500 g	20 min.	24 hours
13a*	90:10	1:1	169.5 c	1.78 p	2.78 pk
13b*	90:10	1:1	16.5 c	3.41 p	4.07 pt
15**	90:10	1:1	2.3 c	0.88 p	2.45 p
16**	100% HEMA	1:1	1.8 c	0.75 p	2.26 p

\*- HEMA/MMA copolymer synthesized in water

\*\* - HEMA/MMA copolymer synthesized in methanol

\*\*\*- poly HEMA synthesized in methanol

## Mode of failure

c=cohesive

p=panel

pk=fiber pick

pt=paper tear

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As Table III shows, poly HEMA/methacrylic acid copolymer prepared in water can also be formulated with a plasticizer, such as polyethylene glycol (PEG), to provide pressure sensitive adhesives. The adhesive performance of the pressure sensitive adhesives can be varied by adjusting the amount of PEG added. The results in Table III also show that the adhesive performance of the pressure sensitive adhesives comprising the poly HEMA/methacrylic acid copolymer prepared in water is comparable to the adhesive performance of pressure sensitive adhesives comprising poly HEMA prepared in alcohol, but without the need for the alcohol solvent.

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As described hereinabove, the copolymer of 2-hydroxyethyl methacrylate and methacrylic acid prepared in water is also useful as abrasion resistant coatings for glass bottles. Tables IV and V, below, show the results of testing performed on glass beer bottles that were coated with the abrasion resistant coating comprising a copolymer of 2-hydroxyethyl methacrylate and methacrylic acid prepared in water according to the method of the present invention.

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Table IV

Abrasion Resistant Coating comprising copolymer

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of polyHEMA/MMA (90/10)

Example	Crosslinker <sup>a</sup>	Surfactant <sup>b</sup>	Wax <sup>c</sup>	Coating Clarity	Scratch Resistance	Water Resistance	Alkali Removal
17	2.5%	0	0	5	4	1	4
18	7.5%	0	0	5	5	3	3
19	2.5%	2%	0	5	4	4	2.5
20	2.5%	0	5%	1	5	4	5
21	7.5%	0	5%	0	5	5	3
22	5%	0	2.5%	0	5	4	5
23	5%	1%	0	5	4	4	5

Rating: 0=worst; 5=best

a=ammonium dichromate

b=Dow Corning 193 silicone surfactant

c=Michem 68725 wax

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Table V

Abrasion Resistant Coating comprising copolymer of polyHEMA/MMA (90/10)

Test	Example No. 24			Example No. 25		
	Initial	1 week, 70°C	3 week, 70°C	Initial	1 week, 70°C	3 week, 70°C
Auto Scratch	Good	Good	Good	OK	OK	OK
Scratch Resistance	5H-6H	6H	6H	5H	6H	6H
Water Resistance						
Initial	OK	OK	OK	OK	OK	OK
1 hour	3H	H	H	3H	3H	3H
Caustic Wash	Good	Good	Good	Good	Good	Good

The auto scratch test is performed by contacting two coated bottles together to facilitate the scratching of the exterior surface of the bottles. The scratch resistance of the coated bottle is measured by using a H to 6H pencil to scratch the exterior surface of the coated bottle. The water resistance of the coated bottle is measured by soaking the coated bottles on deionized water for 48 hours at room temperature. The exterior surface of the soaked bottles are then scratched with an individual's fingernail immediately when taken from the water, or scratched with a H to 6H pencil after one hour of drying at room temperature. The caustic wash test measures the removability of the copolymer coating by alkali treatment. The copolymer coated bottles are placed into a caustic solution, such as 1% sodium hydroxide for 15 minutes at room temperature with magnetic stir bar agitation, followed by rinsing with water.

As Tables IV and V show, that the copolymers of 2-hydroxyethyl methacrylate and methacrylic acid are useful as abrasion resistant coatings for glass bottles. The copolymer coatings prevent scratching of the exterior surface of glass beer bottles, even after soaking in deionized water. In addition, the copolymer coating is easily removed from the exterior surface of the glass bottles by treatment with an alkali solution.

## EXAMPLE 26

## Preparation of Clear Core/Shell Polymer Emulsion

<u>Reactor Charge</u>	<u>grams</u>
Deionized Water	175.7
Airvol 523 (15% solution)	65.0

Disponyl FES 77 (32%)	14.3
NaFeEDTA	0.02
Tert-Butyl Hydroperoxide	0.3

5 Activator Feed

Deionized Water	150.9
Sodium Formaldehyde Sulfoxylate	1.1

Core Feeds

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Water Soluble Monomer Feed

Deionized Water	338.0
2-Hydroxyethyl Methacrylate	160.0
n-Vinyl Pyrrolidone	100.0
tert-Butyl Hydroperoxide	2.0

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PreEmulsion Feed

Deionized Water	105.2
Airvol 523 (15% solution)	32.5
Disponyl FES 77 (32%)	14.3
Butyl Acrylate	100.0
Diethylaminoethyl Methacrylate	40.0

20

Shell Feed

2-Hydroxyethyl Methacrylate	50.0
n-Vinyl Pyrrolidone	31.3
Butyl Acrylate	40.0
Methacrylic Acid	3.8
Tert-Butyl Hydroperoxide	0.1

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Ammonium Hydroxide (28%)	1.9
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Cook Off

Tert-Butyl Hydroperoxide	0.5
Total	1426.8

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PROCEDURE

1. Heated Reactor Charge to 53-55°C with a 55°C jacket. Mixed at 125 RPM and used a nitrogen purge.
- 10 2. Added 15g of PreEmulsion Feed to Reactor.
3. Waited 5 minutes, then added 7g of Activator solution.
4. Waited 5 minutes, then began 3 Feeds:  
15 Monomer: 600g/180min. (=3.33g/min)  
PreEmulsion: 277g/180min. (= 1.54g/min)  
Activator: 145ml/270min. (=0.54ml/min)
5. 20 minutes after Monomer & PreEmulsion feeds ended, began shell feed:  
20 127g/60 (=2.11g/min).
6. Continued Activator feed for 30 minutes after Shell feed ended. Then stopped Activator Feed and added Cook Off.
- 25 7. Cooked for 30 minutes, then cool and discharged.

The resulting polymer had the following properties:

30	Solids	32.5%
	Viscosity	111 cPs

## EXAMPLE 27

## Preparation of Clear Core/Shell Polymer Emulsion

	<u>Reactor Charge</u>	<u>grams</u>
5	Deionized Water	143.0
	Airvol 523 (10% solution)	95.7
	Disponyl FES 77 (32%)	14.3
	NaFeEDTA	0.02
	tert-Butyl Hydroperoxide	0.3
10	<u>Activator Feed</u>	
	Deionized Water	135.9
	Sodium Formaldehyde Sulfoxylate	1.1
15	<u>Core Feeds</u>	
	Monomer Feed	
	Deionized Water	83.0
	2-Hydroxyethyl Methacrylate	80.0
	n-Vinyl Pyrrolidone	30.0
20	tert-Butyl Hydroperoxide	2.0
	PreEmulsion Feed	
	Deionized Water	36.9
	Airvol 523 (10% solution)	48.8
25	Disponyl FES 77 (32%)	14.3
	Butyl Acrylate	63.5
	Methyl Acrylate	9.5
	Methyl Methacrylate	9.5
	Diethylaminoethyl Methacrylate	25.0
30	Trifluoroethyl Methacrylate	2.5

Shell Feed-Monomer

	2-Hydroxyethyl Methacrylate	36.3
	n-vinyl Pyrrolidone	9.9
	Dimethylaminoethyl Acrylate-	7.1
5	Methyl Chloride Quaternary	
	Methacrylic Acid	9.9
	Methyl Acrylate	11.0
	Methyl Methacrylate	33.3
10	Trifluoroethyl Methacrylate	2.5
	tert-Butyl Hydroperoxide	0.2

Shell Feed-Ammonia

	Deionized Water	107.1
15	Ammonium Hydroxide (30%)	5.0

Cook Off

	Tert-Butyl Hydroperoxide	0.5
20	Total	1018.1

PROCEDURE

1. Heated Reactor Charge to 53-55°C with a 55°C jacket. Mixed at 125 RPM and used a nitrogen purge.
2. Added 15g of PreEmulsion Feed to Reactor.
3. Waited 5 minutes, then added 7g of Activator solution.
4. Waited 5 minutes, then began 3 Feeds:  
Monomer: 195g/100min. (=1.95g/min)

PreEmulsion: 195g/100min. (=1.95g/min)

Activator: 130ml/240min. (=0.54ml/min)

5. 20 minutes after Monomer and PreEmulsion feeds ended, began Shell Monomer  
5 feed: 110g/60 min (=1.83g/min) and began Shell Ammonia feed: 110g/60 min  
(=1.83g/min).
6. Continued Activator feed for 30 minutes after Shell feed ended. Then stopped  
Activator Feed and added Cook Off.
- 10 7. Cooked for 30 minutes, then cooled and discharged.

The resulting polymer had the following properties:

	Solids	33.9%
15	Viscosity	300 cPs

#### EXAMPLE 28

Preparation of Copolymer by Alkyl Acrylate Emulsion/Water-Soluble Feeds Method

#### 20 Reactor Charge

	Deionized Water	175.7 g
	Airvol 523 (15% solution)	65 g
	Disponyl FES 77 (32%)	14.3 g
	NaFeEDTA	0.02 g
25	tert-Butyl Hydroperoxide	0.3 g

#### Monomer Feed

	Deionized Water	338 g
	2-Hydroxyethyl Methacrylate	160 g
30	n-Vinyl Pyrrolidone	100 g
	tert-Butyl Hydroperoxide	2 g



## PreEmulsion Feed

	Deionized Water	105.2 g
	Airvol 523 (15% solution)	32.5 g
	Disponyl FES 77 (32%)	14.3 g
5	Butyl Acrylate	100 g
	Diethylaminoethyl Methacrylate	40 g

## Activator Feed

	Deionized Water	135.9 g
10	Sodium Formaldehyde Sulfoxylate	1.1 g

## Cook Off

	tert-Butyl Hydroperoxide	0.5 g
15	Total	1284.8 g

## PROCEDURE

1. The reactor charge was heated to about 53-55°C with a 55°C jacket. Mixed at  
20 125 RPM and used a nitrogen purge.
2. 15 g of PreEmulsion Feed was added to the reactor.
3. After 5 minutes, 7 g of Activator solution was added to the reactor.  
25
4. After 5 minutes, begin to add three feeds:  
Monomer Feed 600 g/210 minutes (2.86 g/min)  
PreEmulsion Feed 277 g/210 minutes (1.32 g/min)  
Activator Feed 130 ml/240 minutes (0.54 ml/min)

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5. Continue to add Activator Feed for 30 minutes after Monomer and PreEmulsion feeds end.

6. Stop adding Activator Feed and add Cook Off.

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7. Cook for 30 minutes, then cool and discharge.

The resulting polymer had the following properties:

	Solids	31.8%
10	Viscosity	78 cPs

Example No. 28 is a poly 2-hydroxyethylmethacrylate copolymer prepared in water emulsions according to the Alkyl Acrylate emulsion/water-soluble feeds method of the present invention. Example Nos. 29-31 are poly 2-hydroxyethylmethacrylate copolymers prepared in water emulsions according to the core/shell method of the present invention. Example Nos. 28-31 were evaluated as coatings for ink jet applications. Example No. 29 of Table VI is the copolymer prepared according to Example No 26 described hereinabove. Example No. 31 of Table VI is the copolymer prepared according to Example No. 27 described hereinabove. The copolymer coatings of the present invention were compared to Comparative Example Nos. 32-35.

The poly 2-hydroxyethyl methacrylate copolymer emulsions of Example Nos. 28-31 were coated onto MYLAR™ clear polyester films (Dupont; Wilmington, Delaware) having a thickness of 4 millimeters (mm) at a coat weight of about 20 to about 25 g/m<sup>2</sup>. The coating was dried at 70°C for about 15 minutes. The clear polyester film having the dried coating thereon was cut into 8 1/2" x 11" sheets for testing.

Comparative Example Nos. 32 and 33 are premium inkjet transparency films for overhead projectors that are commercially available from Hewlett Packard

- Company (Palo Alto, California) and Minnesota Mining and Manufacturing Company (3M; Saint Paul, Minnesota). Comparative Example No. 34 is a premium glossy paper for inkjet printer that comprises a clear polyester film with an opaque coating thereon that is commercially available from Hewlett Packard Company.
- 5 Comparative Example No. 35 is a plain clear polyester film without a coating.

The poly 2-hydroxyethyl methacrylate copolymer coatings were evaluated for clarity, image quality, drying time, ink density, and water resistance. Each property was evaluated on a scale from 1 to 5, with 1 being the lowest possible  
10 rating and 5 being the highest possible rating.

The clarity was evaluated by a visual inspection of the coated film before printing for haziness and particulate matter.

- 15 The image quality was evaluated by a visual inspection performed after printing. The visual inspection was performed using a 10X magnifying glass, looking for indications of "feathering", which represents fuzzy edges of images, "mud cracking", and "cascading", which is a measure of the coverage in the fill areas.

20

The ink density was measured after printing using a densitometer (Tobias IQ 150 portable reflection densitometer) in a 100% fill area of each color. The units for ink density are density units.

- 25 The drying time of the ink on the coated films was measured immediately after the printing was completed. The dry time was tested by testing the smearing of the various colors on the film every 30 seconds until the ink dried. The time indicated in Table VI is the time for the last color to smear. Although the testing was performed on film, it is important to note that the acrylic emulsion ink jet  
30 receptive coatings of the present invention are also useful as glossy coatings on paper that is to be utilized for ink jet printing.

The water resistance was tested about 20 minutes after the printing was completed. Each example was held at an angle while about 5 ml of water was dripped onto the 100% fill area of each color. The results of the above described tests are set forth in Table VI, below.

5

TABLE VI

Evaluation of 2-hydroxyethyl methacrylate copolymers as ink jet coatings

Example No.	28	29	30	31	C32	C33	C34	C35
Coat Weight	25	19	22	21	---	---	---	---
Clarity*	4	4	4.5	3	1	2	opaque	5
Image Quality*	3	3	3.5	3.5	3	3	4	1
Ink Density								
Black	0.82	0.88	1.42	1.42	1.82	2.04	1.76	0.34
Cyan	0.74	0.76	0.87	0.85	0.70	0.72	0.71	0.96
Magenta	1.74	1.82	1.88	1.82	1.45	1.59	1.33	1.17
Yellow	1.2	1.19	1.25	1.25	1.25	1.19	1.29	0.21
Drying Time, minutes	3	3	2	2	1.5	1.5	1	1200
Water Resistance*	2	2.5	4	4	2	1	3	1

\* 1(worst)- 5 (best)

10 Comparative Example Nos. C32 and C33 are commercially available ink jet transparency films having a grainy appearance. Comparative Example No. C34 is a commercially available ink jet paper that is a pigmented film. Comparative Example No. C35 is a commercially available plain polyester film without a coating, which does not absorb or dry ink. As one can see from Table VI, the hydrophilic emulsions of the present invention are particularly useful as clear coatings for ink jet recording films. The clear coatings provide excellent performance without the need for the addition of pigments and, therefore, avoids the grainy/hazy appearance associated with the commercially available films.

20

## EXAMPLE 36

## Preparation of poly(HEMA) Powder

## Recipe (100 gram batch)

The following were added to a reaction vessel with stirring:

25	Deionized Water	60.0 g
	2-Hydroxyethyl Methacrylate (Mitsubishi)	30.0 g

After 15 minutes of a nitrogen purge, the following was added:

Sodium Metabisulfite (10% solution)	5.0 g
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After an additional 15 minutes of a nitrogen purge, the following was added:

Sodium Metabisulfite (10% solution)	5.0 g
-------------------------------------	-------

5

The reaction was held at ambient temperature for an additional 4 hours with a constant nitrogen flow. The product was chopped and leached overnight, then dried. The dried product was ground up into a powder (about 50 microns). The product synthesized in Example No. 36, above, exhibited 9.7%, gel as determined  
10 by the gel content method described hereinabove.

The powder (25 g) was compounded with PEG 400 polyethylene glycol (25 g) to form a pressure-sensitive adhesive. PEG 400 polyethylene glycol is commercially available from Union Carbide under the trade designation Carbowax®,  
15 Sentry Grade, Polyethylene Glycol 400.

The tack of the pressure sensitive adhesive was determined by a modified spherical probe adhesion test that involves recording and analyzing the entire stress-strain behavior of a pressure sensitive adhesive during bonding and debonding of the  
20 probe. The test apparatus consists of a stainless steel spherical probe connected to a force transducer. The force transducer measures the force acting upon the spherical probe. The probe is moved up and down by a rotating screw driven by a stepping motor. A pressure sensitive adhesive sample is bonded adhesive side up to the test platform with a double-sided tape. During bonding of the probe to the pressure  
25 sensitive adhesive, the probe moves down and compresses the adhesive to a pre-determined force (i.e.- compression force). During the debonding process, the probe ascends and separates from the pressure sensitive adhesive sample and a pre-determined test speed. As the probe ascends, the adhesive sample becomes elongated and exerts a tensile force on the transducer. As the adhesive is further  
30 elongated, the stress increases in the adhesive until it reaches the interfacial strength between the probe and the adhesive, at which point the probe separates from the

adhesive sample. The debonding strength of the adhesive sample is measured by the magnitude of the force and duration time of the probe. The pressure sensitive adhesive of Example No. 36 exhibited a tack value of 0.2303 N Force and 93.965 Nm ( $\times 10^{-5}$ ) Energy. For a detailed description for the measurement of the tack of pressure sensitive adhesives, see "Avery Adhesive Test, AAT", Adhesives Age, Vol. 10, No. 10, pp.18-23 (1997).

Example Nos. 37-45 are examples of 1-1.5 mm thick pressure sensitive adhesives comprising poly 2-hydroxyethyl methacrylate powders blended with polyethylene glycol (PEG) 400 at a powder:PEG ratio of 1:2. The poly 2-hydroxyethyl methacrylate powders were prepared using different HEMA monomer sources. The tack and rheometrics of the pressure sensitive adhesives are reported in Table VIIa, below.

TABLE VIIa  
Pressure Sensitive Adhesives of  
poly 2-hydroxyethyl methacrylate and polyethylene glycol

Ex.	% INT/ACT	%Gel	Force (N)	Energy Nm( $10^{-5}$ )	Rheometrics			
					G' 0.1 rad/s dyne/cm $\times 10^4$	G' 100 rad/s dyne/cm $\times 10^4$	G'' 0.1 rad/s dyne/cm $\times 10^4$	G'' 100 rad/s dyne/cm $\times 10^4$
37*	0.1	98.5	0.1312	3.4189	17.8420	2.0629	33.9930	6.7337
38*	0.8	85.8	0.1827	15.0930	4.3926	0.7101	13.9110	5.0524
39*	1.6	76.5	0.1535	17.6360	1.8554	0.3791	8.6069	4.4009
40**	0.1	97.1	0.2215	6.2883	17.2500	2.6183	31.8970	5.3206
41**	0.8	63.8	0.1332	67.8080	0.8932	0.6411	10.5470	5.0334
42**	1.6	14.8	0.0531	153.7300	0.0817	0.1560	6.3956	4.6835
43***	0.1	96.7	0.1476	4.4343	2.8014	0.3687	5.4282	1.0169
44***	0.8	73.5	0.1757	33.4000	3.2641	1.0506	18.8390	8.1289
45***	1.6	59.2	0.0500	22.6810	0.2321	0.1943	6.6193	5.1477

HEMA sources: \*Rohm & Haas OGM, \*\* Mitsubishi SEC, \*\*\*RohmTech BM 903

Table VIIa shows poly HEMA powder prepared with various sources of HEMA monomers, and various ratios of initiator/activator can be formulated with polyethylene glycol to form a pressure sensitive adhesive. The pressure sensitive adhesives have good adhesive performance (i.e.- high Force and Energy as measured by the ATT test described hereinabove).

Example No. 46-54 in Table VIIb are examples of pressure sensitive adhesives comprising poly 2-hydroxyethyl methacrylate powders blended with polyethylene glycol (PEG) 400 at powder:PEG ratios of 1:1, 1:2 and 1:3. The poly 2-hydroxyethyl methacrylate powders were prepared with HEMA monomers commercially available from Mitsubishi. The tack, including Force (N) and Energy (Nm x 10<sup>-5</sup>) of the pressure sensitive adhesives are reported in Table VIIb, below.

TABLE VIIb

Pressure Sensitive Adhesives of  
poly 2-hydroxyethyl methacrylate\* and polyethylene glycol

Example*	%INT/ACT			Force (N)	Energy Nm(x 10 <sup>-5</sup> )
		%Gel	Powder:PEG		
46	0.1	95.7	1:1	0.1504	2.8897
47	0.8	66.2	1:1	0.2626	14.8660
48	1.6	9.7	1:1	0.2303	93.9650
49	0.1	97.1	1:2	0.2215	6.2883
50	0.8	63.8	1:2	0.1332	67.8080
51	1.6	14.8	1:2	0.0531	153.7300
52	0.1	95.7	1:3	0.1184	4.1229
53	0.8	66.2	1:3	0.0450	21.1301
54	1.6	9.7	1:3	elongation too high	

\*Mitsubishi SEC

Table VIIb shows that low gel polyHEMA powder prepared with the Mitsubishi HEMA monomers formulated with lower levels polyethylene glycol provides the highest ATT values. Because of the low gel content of the polyHEMA powder, it is possible to reduce the amount of plasticizer used to prepare a pressure sensitive adhesive.

Example Nos. 55-61 in Table VIII are poly 2-hydroxyethyl methacrylate polymers prepared by blending 2-hydroxyethyl methacrylate monomers having less than 3 weight percent alkylene glycol methacrylate impurities and containing 0.05-0.1% by weight of ethylene glycol dimethacrylate with 2-hydroxyethyl methacrylate monomers having less than 3 weight percent alkylene glycol methacrylate impurities and greater than 0.15% by weight of ethylene glycol dimethacrylate. The poly

HEMA powders were formulated with PEG at a ratio of one part poly HEMA powder to two parts PEG plasticizer. As shown in Table VIII, poly 2-hydroxyethyl methacrylate prepared according to the present invention having a %INT/ACT from about 0.1 to about 1.6 exhibit a Force of about 0.12 N to about 0.2 N and an  
 5 Energy of about 4.7 Nm ( $\times 10^{-5}$ ) to about 40 Nm ( $\times 10^{-5}$ ).

The rheometrics for the poly 2-hydroxyethyl methacrylate was also evaluated. A detailed description relating to the measurement of modulus is provided in "Viscoelastic Windows of Pressure-Sensitive Adhesives", E.P. Chang,  
 10 J. Adhesion, Vol. 34 pp. 189-200 (1991), and "Viscoelastic Properties of Pressure-Sensitive Adhesives", E.P. Chang, J. Adhesion, Vol. 60 pp. 233-248, (1997). Briefly, dynamic shear modulus (G) can be resolved into components of storage modulus (G') plus dissipation modulus (G''). In dynamic mechanical testing with  
 15 varying amplitude and frequency, sinusoidal deformation is applied to the test sample and the resultant torque or force transmitted through the sample to a transducer is measured. Both the strain and the torque signals are amplified and input to a central processing unit where the phase angle between the strain and torque and the dynamic modulus are calculated using programs related to the test mode and sample geometry selected.

20

TABLE VIII

Ex.	HEMA OGM*:SEC**	% INT/ACT	%Gel	Avery Tack		Rheometrics dyne/cm $\times 10^4$			
				Force (N)	Energy Nm( $10^{-5}$ )	G' 0.1 rad/s	G' 100 rad/s	G'' 0.1 rad/s	G'' 100 rad/s
55	50:50	0.1	93.3	0.1391	4.719	17.0220	30.8500	2.2762	5.1992
56	50:50	0.8	75.8	0.1999	26.223	2.8982	12.8910	0.8750	4.8199
57	50:50	1.6	58.9	0.1290	39.340	0.5618	5.5776	0.2443	3.1655
58	75:25	0.1	92.0	0.1464	4.998	6.5796	13.2500	0.9310	2.6070
59	75:25	0.8	79.7	0.1560	14.257	5.2057	17.9140	1.1070	5.9671
60	75:25	0.8	78.8	0.1675	15.706	5.8394	20.0840	1.2593	6.8274
61	75:25	1.6	62.2	0.1647	24.573	1.4052	9.5499	0.4508	5.0231

\* Mitsubishi SEC

\*\* Rohm &amp; Haas Rocryl OGM

25



Table VIII shows that pressure sensitive adhesives having adequate ATT performance can be prepared using a combination of low gel producing HEMA monomers (Mitsubishi) and high gel producing HEMA monomers (Rohm & Haas).

5

**EXAMPLE 62****Preparation of HEMA/4-HBA Copolymer in Alcohol**

Recipe (1003.75g batch)

10 Reactor Charge

2-Hydroxyethyl Methacrylate (Mitsubishi)	150 g
4-Hydroxybutyl Acrylate (4-HBA)	150 g
Ethanol	600 g
Benzoyl Peroxide	1.5 g

15

Cook-Off Initiator #1

Ethanol	33.3 g
AIBN (2,2'-azobis[isobutyronitrile])	0.75 g

20 Cook-Off Initiator #2

Ethanol	33.3 g
AIBN (2,2'-azobis[isobutyronitrile])	0.75 g

Cook-Off Initiator #3

25	Ethanol	33.3 g
	AIBN (2,2'-azobis[isobutyronitrile])	0.75 g

PROCEDURE

1. The Reactor Charge was weighed out into a flask and poured into a reaction kettle with mixing, heated with a 80°C jacket, and N<sub>2</sub> purged.
- 5 2. The Cook-Off Initiator #1 (Ethanol and AIBN) was weighed into a small beaker and mixed until the solids dissolved.
3. Three and one-half hours after adding the Reactor Charge, the Cook-Off  
10 Initiator #1 was poured into the reaction kettle.
4. Cook-Off Initiator #2 (Ethanol and AIBN) was weighed into a small beaker and mixed until the solids dissolved.
- 15 5. One hour after adding Cook-Off #1, Cook-Off #2 was added.
6. Cook-Off Initiator #3 (Ethanol and AIBN) was weighed into a small beaker and mixed until the solids dissolved.
- 20 7. One hour after adding Cook-Off #2, Cook-Off #3 was added.
8. One hour after adding Cook-Off #3, the kettle contents were cooled, then discharged into a quart jar.
- 25 The copolymer product synthesized in Example No. 14, above, exhibited the following properties:

Appearance: clear, light yellow gel-free liquid.

Solids: 30.5%

Viscosity: 844 cPs

Residual monomer: HEMA <0.01%, 4-HBA 0.22%

5 Glass Transition Temperature,  $T_g$ ,  $^{\circ}\text{C}$

% Gel in water: 98%

The copolymer is swellable in water up to twice its weight.

Examples 63-70 are copolymers of 2-hydroxyethyl methacrylate and 4-  
10 hydroxybutyl acrylate having varying ratios of 2-hydroxyethyl methacrylate to 4-  
hydroxybutyl acrylate, and which were prepared substantially in accordance with the  
procedure of Example 62. The moisture vapor transmission rate (MVTR) and  
mechanical properties, including % strain at peak, stress at peak, stress at 2%  
elongation, and Young's modulus, of the copolymers of 2-hydroxyethyl  
15 methacrylate and 4-hydroxybutyl acrylate were tested. The results of the evaluation  
of the moisture vapor transmission rate and mechanical properties are shown in  
Table IXa.

Moisture Vapor Transmission Rate (MVTR) is a measure to describe the  
20 ability of a film to allow moisture vapor to pass through over specific period of time  
and under a controlled temperature and atmospheric pressure. With particular  
reference to skin applications, such as protective films and coatings, the MVTR is a  
measure of a film's ability to move vapor away from the skin of a patient. The  
MVTR was measured according to INDA Standard IST 70.4 (99). The samples  
25 were coated on a 1 mil thick MVTR film commercially available from Mylan  
Technologies (St. Albans, VT; U.S.A.) under the designation Medifilm 390 at a  
coat weight of 25 to 35 g/m<sup>2</sup>.

TABLE IXa

Example	Ratio HEMA/ 4HBA	T <sub>g</sub>	Tensile Testing				MVTR g/m <sup>2</sup> /day
			% Strain at peak	Stress at peak (psi)	Stress at 2% yield (psi)	Young's Modulus (psi)	
63	50/50	5°C	too soft	---	---	---	3440
64	60/40	20°C	266	1035	216	5,585	2880
65	67/33	26°C	166	1618	910	38,211	2590
66	70/30	29°C	6.7	2142	1583	59,657	1980
67	75/25	36°C	4.9	4026	2520	145,714	1920
68	80/20	54°C	too brittle	---	---	---	2650
69	100/0	70°C	too brittle	---	---	---	2156
70	0/100	-30°C	---	---	---	---	4330

Coatings of the copolymers of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate were also evaluated for abrasion resistance of the coating to cloth to simulate the abrasion resistance of the copolymer to clothing.

The abrasion resistance of the copolymers of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate of Examples 63-70, prepared in accordance with the methods of the present invention, were evaluated for abrasion resistance by a modified Southerland Rub Test (ASTM D1331-89). The results of the abrasion resistance studies are set forth in Table IXb.

TABLE IXb

Example	Ratio HEMA/4HBA	Southerland Rub Test 4 lbs, 200 strokes	
		Coating against coating	Coating against cloth
63	50/50	failed, too tacky	slight abrasion
64	60/40	few scratches	slight abrasion
65	67/33	scratches & abrasion	slight abrasion
66	70/30	scratches & abrasion	no abrasion
67	75/25	scratches & abrasion	slight abrasion
68	80/20	scratches & abrasion	slight abrasion
69	100/0	scratches & abrasion	slight abrasion

As shown in Table IXb, above, coatings comprising a copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate, prepared in accordance with the methods of the present invention, exhibit only slight abrasion when rubbed against cloth and, therefore, appear useful as skin coatings or barriers.

5

The surface tension of copolymers of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate and copolymers of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate containing 0.1%, 0.2%, 0.5% or 1% of a silicone surfactant were determined and compared to the surface tensions of water and ethanol. The results of the surface tension testing is set forth in Table IXc.

10

TABLE IXb  
Surface Tension

Example No.		Surface Tension dynes/cm
71	water	74.1
72	ethanol	24.1
73	copolymer of 2-HEMA/4-HBA	30.4
74a	copolymer of 2-HEMA/4-HBA 0.1 % surfactant	26
74b	copolymer of 2-HEMA/4-HBA 0.2 % surfactant	24.1
74c	copolymer of 2-HEMA/4-HBA 0.5 % surfactant	23.9
74d	copolymer of 2-HEMA/4-HBA 1 % surfactant	23.3

15

As shown in Table IXc, above, the copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate has a surface tension of about 30 dynes/cm. The addition of at 0.1% of a silicon surfactant to the copolymer of 2-

hydroxyethyl methacrylate and 4-hydroxybutyl acrylate reduces the surface tension of the copolymer to 26 dynes/cm or lower.

In general, to "wet" a surface, it is necessary to use a material that has a surface tension that is similar to and, preferably, lower than the surface tension of the surface to be "wetted." Human skin has a surface tension of about 27 dynes/cm. To "wet" the surface of human skin, it is necessary to utilize a material that possesses a surface tension that is similar than the surface tension of human skin. Using a copolymer 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate, it is possible to provide a continuous copolymer coating for the surface of human skin without experiencing bleeding or gaps therein.

#### EXAMPLE 75

Preparation of copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate in an ethanol/water solution.

Recipe (1002.4 gram batch)

##### Reactor Charge

	2-Hydroxyethyl Methacrylate (Mitsubishi)	200 grams
20	4-Hydroxybutyl acrylate	100 grams
	Ethanol	400 grams
	Deionized Water	260 grams

##### Initiator Charge

25	Deionized Water	10 grams
	Sodium Persulfate (0.5%)	1.5 grams

##### Cook-Off Initiator #1

	Deionized Water	10 grams
30	Sodium Persulfate	0.3 grams

## Cook off Initiator #2

Deionized Water	10 grams
Sodium Persulfate	0.3 grams

## 5 Cook off Initiator #3

Deionized Water	10 grams
Sodium Metabisulfite	0.3 grams

Total	1002.4 grams
-------	--------------

10

PROCEDURE

1. The Reactor Charge was weighed out into a flask and poured into a reaction kettle with mixing, and was heated with an 80°C jacket and a N<sub>2</sub> purge kettle.

15

2. The Cook-Off initiator #1 was weighed into a small beaker and mixed until the solids dissolved.

3. About three hours after the addition of the Reactor Charge, Cook-Off initiator #1 was added to the kettle.

20

4. The Cook-Off initiator #2 was weighed into a small beaker and mixed until the solids dissolved.

5. About one hour after the addition of Cook-Off initiator #1, Cook-Off initiator #2 was added to the kettle.

25

6. The Cook-Off initiator #3 was weighed into a small beaker and mixed until the solids dissolved.

30

7. One hour after the addition of Cook-Off initiator #2, Cook-Off initiator #3 was added to the kettle.

8. About one-half hour after the addition of Cook-Off initiator #3, the kettle contents were cooled and discharged.

The polymeric product synthesized in Example No. 14, above, exhibited the following properties:

10 Appearance: clear to light-yellow gel-free liquid

Solids: 30%

Residual monomers

2-Hydroxyethyl Methacrylate	0.02%
-----------------------------	-------

4-Hydroxybutyl Acrylate	<0.01%
-------------------------	--------

15

Pressure sensitive adhesives were prepared comprising either the homopolymer of poly-4-hydroxybutyl acrylate prepared in an alcohol/water mixture, a homopolymer of poly-2-hydroxyethyl methacrylate prepared in an alcohol/water mixture, or a copolymer of poly-2-hydroxyethyl methacrylate and poly-4-hydroxybutyl acrylate prepared in an alcohol/water mixture as described above.

Each of the pressure sensitive adhesive compositions were evaluated for static shear properties and peel adhesion properties on stainless steel substrates and polymeric substrates, such as high density polyethylene (HDPE). The results of the tests are shown in Table Xa.



TABLE Xa

Ex.	HEMA/ 4-HBA	Polymer/ PEG	Shear, min. $\frac{1}{4}$ in <sup>2</sup> . 500g	180° Peel, lb/in 15 min., SS	180° Peel, lb/in 15 min., HDPE	180° Peel, lb/in 24 hr., SS	180° Peel, lb/in 24 hr, HDPE
76	0/100	100/0	4,260 (+)	3.423 (ft)	0.695 (cl)	4,187 (ft)	2.165 (cl)
77	50/50	75/25	63.4 (sp)	3.391 (cl)	1.116 (cl)	3.761 (cl)	0.937 (cl)
78	100/0	60/40	223.4 (sp)	2.973 (cl)	0.466 (cl)	3.042 (ft)	0.865 (cl)

The tack of the pressure sensitive adhesive was determined by a modified spherical probe adhesion test that involves recording and analyzing the entire stress-strain behavior of a pressure sensitive adhesive during bonding and debonding of the probe. The test apparatus consists of a stainless steel spherical probe connected to a force transducer. The force transducer measures the force acting upon the spherical probe. The probe is moved up and down by a rotating screw driven by a stepping motor. A pressure sensitive adhesive sample is bonded adhesive side up to the test platform with a double-sided tape. During bonding of the probe to the pressure sensitive adhesive, the probe moves down and compresses the adhesive to a pre-determined force (i.e.- compression force). During the debonding process, the probe ascends and separates from the pressure sensitive adhesive sample and a pre-determined test speed. As the probe ascends, the adhesive sample becomes elongated and exerts a tensile force on the transducer. As the adhesive is further elongated, the stress increases in the adhesive until it reaches the interfacial strength between the probe and the adhesive, at which point the probe separates from the adhesive sample. The debonding strength of the adhesive sample is measured by the magnitude of the force and duration time of the probe. The results of the tests are shown in Table Xb, below. For a detailed description for the measurement of the tack of pressure sensitive adhesives, see "Avery Adhesive Test, AAT", Adhesives Age, Vol. 10, No. 10, pp.18-23 (1997).

TABLE Xb

Ex.	HEMA/ 4-HBA Copolymer	Polymer/PEG	Force (N)	Energy Nm x 10 <sup>-5</sup>
76	0/100	100/0	0.977	0.144
77	50/50	75/25	1.359	0.079
78	100/0	60/40	1.089	0.024

As described hereinabove, the copolymers of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate prepared according to the method of the present invention possess the capability to undergo self crosslinking with thermal treatment. Examples 78-82 are copolymers of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate prepared in ethanol, where the ratio of HEMA to 4-HBA is 67/33. Examples 84-87 are copolymers of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate prepared in a solution of ethanol and water, where the ratio of HEMA to 4-HBA is 60/40. Examples 88-90 are copolymers of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate prepared in a solution of ethanol and water, where the ratio of HEMA to 4-HBA is 50/50. All of the copolymer products were cast into films and the films were dried at 70°C for 15 minutes. Thereafter, the percent(%) insoluble, percent (%) strain at break, and Young's modulus were tested for each copolymer product. Comparative Examples 79, 81, and 85 were dried at 70°C for 15 minutes, but were not cured further.

The strain of a particular body refers to the change in the dimensions of that body in response to an applied force. The Young's modulus of a particular body refers to the ratio between the compressive stress and the elongation of a solid body. The % strain at break and the Young's modulus of the copolymers of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate were determined according to ASTM Standard D 638M (93) using dumbbell-shaped test samples.

The results of the tensile testing and percent insoluble in methanol of samples are reported in Table XI below.

TABLE XI

5

Ex.	HEMA/ 4-HBA ratio	Curing conditions	Tensile Testing		% insoluble in MeOH
			% Strain at break	Young's Modulus, psi	
C79	67/33	---	253.5	17227	33.8
80	67/33	100°C, 5 min	195.3	23489	56.8
81	67/33	125°C, 5 min	184.2	31192	67.1
82	67/33	150°C, 5 min	150	59470	89.7
C83	60/40	---	399.4	500.2	59.3
84	60/40	100°C, 5 min	383.4	1499.6	60.6
85	60/40	125°C, 5 min	342.7	3917.4	59.1
86	60/40	150°C, 5 min	328.8	5514.1	75.3
C87	50/50	---	564.9	89	53.1
88	50/50	100°C, 5 min	524.9	193.5	61.6
89	50/50	125°C, 5 min	495.3	148.6	72
90	50/50	150°C, 5 min	356.8	449.3	83

As shown in Table XI, the copolymers of HEMA and 4-HBA can be self-crosslinked with thermal treatment only. The cured copolymers exhibit lower strains at break and higher moduli as compared to the uncured copolymers. The ability to self crosslink is especially beneficial where the copolymeric product is intended to be utilized for skin applications and, therefore, it would be advantageous to avoid the use crosslinking agents that may be toxic.

## EXAMPLE 91

Preparation of copolymer of 2-hydroxyethyl methacrylate and  
4-hydroxybutyl acrylate in an ethanol/water solution.

## 5 Recipe

Reactor Charge

	2-Hydroxyethyl Methacrylate (Mitsubishi)	16.64 Kg
	4-Hydroxybutyl acrylate	8.32 Kg
	Ethanol	24.12 Kg
10	Deionized Water	24.12 Kg

Initiator Charge

	Deionized Water	0.41 Kg
	Sodium Persulfate	0.13 Kg

15

Cook-Off Initiator #1

	Deionized Water	0.2 Kg
	Ethanol	0.2 Kg
	Sodium Persulfate	0.025 Kg

20

## Cook off Initiator #2

	Deionized Water	0.2 Kg
	Ethanol	0.2 Kg
	Sodium Persulfate	0.025 Kg

25

## Cook off Initiator #3

	Deionized Water	0.2 Kg
	Ethanol	0.2 Kg
	Sodium Metabisulfite	0.025 Kg

30

	Total	75.4 Kg
--	-------	---------

PROCEDURE

1. Begin heating reactor with a 83°C jacket and with a N<sub>2</sub> purge.
- 5 2. The Reactor Charge was weighed out into a weight tank and transferred to the reactor with mixing.
3. When Reactor Charge reaches a temperature of about 76°C, the Initiator Charge was added to the reactor.
- 10 4. With reaction temperature going to 85°C. Start hold period. Hold for three hours (reaction to 77.5°C).
5. The Cook-Off initiator #1 was weighed into a beaker, and mixed until the  
15 solids dissolved.
6. About three hours after the addition of the Reactor Charge, Cook-Off initiator #1 was added to the reactor.
- 20 7. The Cook-Off initiator #2 was weighed into a beaker and mixed until the solids dissolved.
8. About one hour after the addition of Cook-Off initiator #1, Cook-Off initiator #2 was added to the reactor.
- 25 9. The Cook-Off initiator #3 was weighed into a beaker and mixed until the solids dissolved.
10. One hour after the addition of Cook-Off initiator #2, Cook-Off initiator #3  
30 was added to the reactor.

11. About one hour after the addition of Cook-Off initiator #3, the reactor contents were cooled and the leaching process started.

Samples of the polymerization product were taken from the reactor every hour throughout the reaction to evaluate the conversion of the monomers to the copolymeric product and the residual monomers remaining in the reactor. The amount of the residual monomers remaining in the reactor after each hour of the reaction are shown in Table VI below.

10

TABLE XII

Hour	Residual Monomer	
	HEMA	4-HBA
1	0.25%	0.45%
2	82 ppm	700 ppm
3	85 ppm	360 ppm
4	90 ppm	120 ppm
5	80 ppm	50 ppm
6	50 ppm	< 10 ppm

As is shown in Table XII, one hour after the addition of Cook-Off Initiator #3, the reaction mixture only contains 55 ppm HEMA residual monomer and < 10 ppm 4-HBA residual monomer. These results demonstrate that the copolymerization of HEMA and 4-HBA in a solution of alcohol and water results in a very efficient conversion of monomer into copolymer product with a very low occurrence of residual monomer in the final copolymeric product.

It should be noted that a leaching process may also be utilized to remove any residual monomers and initiators, thus further purifying the copolymeric product of HEMA and 4-HBA. A suitable leaching process for use with the polymer prepared according the present invention is set forth below.

## LEACHING PROCESS

## First Leach

	Water to precipitate polymer	94.1 Kg
5	Decant off effluent	93.3 Kg
	Ethanol to redissolve	7.5 Kg

## Residual monomer remaining after first leach:

	HEMA	< 50 ppm
10	4-HBA	< 10 ppm

## Second Leach

	Water to precipitate polymer	74.8 Kg
	Decant off effluent	92.9 Kg
15	Ethanol to redissolve	7.5 Kg

## Residual monomer remaining after second leach:

	HEMA	< 50 ppm
	4-HBA	< 10 ppm
20		

## Third Leach

	Water to precipitate polymer	74.8 Kg
	Decant off effluent	81.5 Kg
	Ethanol to redissolve	9.4 Kg
25		

## Residual monomer remaining after first leach:

	HEMA	< 50 ppm
	4-HBA	< 10 ppm

30        The leached polymeric product synthesized in Example No. 91, above, exhibited the following properties:

	Viscosity, cPs	660
	% Solids content	23.6%
	% Ethanol	23.5%
	% Water	52.9%
5	Residual monomers	
	2-Hydroxyethyl Methacrylate	< 50 ppm
	4-Hydroxybutyl Acrylate	< 10 ppm

Extensive leaching processes have been conventionally used in the art to  
10 remove residual monomers, initiators, and other reactants from the final polymeric  
products require the use of elevated temperatures, reduced pressures, centrifugation  
and/or multiple washes. To the contrary, all of the polymeric products prepared by  
the methods of the present invention have very low levels of residual monomers and  
other reactants remaining after the polymerization process. However, if further  
15 purification is desired, the polymeric products may be subjected to a leaching  
process with water and ambient temperature and pressure.

While the invention has been explained in relation to its preferred  
embodiments, it is to be understood that various modifications thereof will become  
20 apparent to those skilled in the art upon reading the specification. Therefore, it is to  
be understood that the invention disclosed herein is intended to cover such  
modifications as fall within the scope of the appended claims.



## WE CLAIM:

1. A method for the preparation of a substantially gel-free polymer comprising one of the following:

5 (i) wherein the polymer is a homopolymer of poly 2-hydroxyethyl methacrylate prepared substantially in the absence of a chain transfer agent and wherein the method comprises

introducing monomeric 2-hydroxyethyl methacrylate containing ethylene glycol dimethacrylate impurities in the range of about 0.05 to about 0.1 % by weight  
10 of the monomer into alcohol, and

polymerizing the 2-hydroxyethyl methacrylate to form a polymerization mixture, and optionally

removing the alcohol;

(ii) wherein the polymer is a substantially low gel poly 2-hydroxyethyl  
15 methacrylate prepared substantially in the absence of a chain transfer agent and wherein the method comprises:

introducing monomeric 2-hydroxyethyl methacrylate containing ethylene glycol dimethacrylate impurities in the range of about 0.05 to about 0.1 % by weight  
of the monomer into water; and

20 polymerizing the 2-hydroxyethyl methacrylate to form a polymerization mixture;

(iii) wherein the polymer is a substantially gel free, hydrophilic, water soluble polymer comprising a copolymer of 2-hydroxyethyl methacrylate and acrylic acid or methacrylic acid and wherein the method comprises:

25 introducing monomeric 2-hydroxyethyl methacrylate into water solution with at least one of acrylic acid and methacrylic acid,

adjusting the pH of the solution to a pH in the range of greater than about pH  
3 to less than about pH 9, and

30 copolymerizing the monomeric 2-hydroxyethyl methacrylate and acrylic or methacrylic acid;

(iv) wherein the polymer is a gel free hydrophilic polymer comprising a copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate prepared substantially in the absence of a chain transfer agent and wherein the method comprises:

- 5       introducing monomeric 2-hydroxyethyl methacrylate containing ethylene glycol dimethacrylate impurities in the range of about 0.05 to about 0.1% by weight of the monomer into an alcohol solution with 4-hydroxybutyl acrylate, copolymerizing said 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate to form a polymerization mixture, and
- 10       removing the alcohol;

(v) wherein the polymer is a substantially gel-free copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate prepared substantially in the absence of a chain transfer agent and wherein the method comprises:

- 15       introducing monomeric 2-hydroxyethyl methacrylate containing ethylene glycol dimethacrylate impurities in the range of about 0.05 to 0.1% by weight with monomeric 4-hydroxybutyl acrylate into a solution of water and alcohol; and
- copolymerizing the 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate to form a polymerization mixture;

- (vi) wherein the polymer is a gel-free homopolymer of 2-hydroxyethyl
- 20   methacrylate prepared substantially in the absence of a chain transfer agent and wherein the method comprises:

- introducing monomeric 2-hydroxyethyl methacrylate containing ethylene glycol dimethacrylate impurities in the range of about 0.05 to 0.1% by weight into a solution of water and alcohol; and
- 25       polymerizing the 2-hydroxyethyl methacrylate to form a polymerization mixture;

(vii) wherein the polymer is a gel-free copolymer of 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate prepared substantially in the absence of a chain transfer agent and wherein the method comprises:

- introducing monomeric 2-hydroxyethyl methacrylate containing ethylene glycol dimethacrylate impurities in the range of about 0.05 to 0.1% by weight with monomeric 4-hydroxybutyl acrylate into an alcohol; and
- copolymerizing the 2-hydroxyethyl methacrylate and 4-hydroxybutyl acrylate to form a polymerization mixture; and
- (viii) wherein the polymer is a gel-free homopolymer of 4-hydroxybutyl acrylate prepared substantially in the absence of a chain transfer agent and wherein the method comprises:
- introducing monomeric 4-hydroxybutyl acrylate into alcohol; and
- polymerizing the 4-hydroxybutyl acrylate to form a polymerization mixture.

2. The method of claim 1, wherein the polymer is a substantially low gel poly 2-hydroxyethyl methacrylate prepared substantially in the absence of a chain transfer agent and wherein the method comprises:

- introducing monomeric 2-hydroxyethyl methacrylate containing ethylene glycol dimethacrylate impurities in the range of about 0.05 to about 0.1% by weight of the monomer into water; and
- polymerizing the 2-hydroxyethyl methacrylate to form a polymerization mixture; drying said polymerization mixture; and grinding said dried mixture to form a powder.

3. The method of claims 1 or 2, wherein the monomeric 2-hydroxyethyl methacrylate, if present, contains impurities in a total amount of no more than about 3% by weight of the monomer, and wherein the impurities are selected from the group consisting of ethylene glycol dimethacrylate, diethylene glycol monomethacrylate, methacrylic acid and mixtures thereof.

4. The method of claims 1 or 2, including adding a polyalkylene glycol to the polymerization mixture prior to removing one of (i) the alcohol, (ii) the water, and (iii) the solution of alcohol and water, to form a hydrophilic pressure sensitive adhesive upon removing said alcohol.

5. The method of claim 4, wherein the polyalkylene glycol is selected from the group consisting of polyethylene glycol, polypropylene glycol and copolymers of ethylene glycol and propylene glycol, and mixtures thereof.
- 5
6. The method of claim 1, including adding glycerin to the polymerization mixture of (i)-(viii) prior to removing one of (i) the alcohol, (ii) the water, and (iii) the solution of water and alcohol, and removing (i) the alcohol, (ii) the water, or (iii) the solution of water and alcohol by drying to form a flexible hydrophilic coating.
- 10
7. The method of claim 1, wherein the alcohol, if present, is selected from the group consisting of methanol and ethanol.
- 15
8. The method of claim 5, wherein the polyalkylene glycol is polyethylene glycol.
9. A method of coating a substrate comprising applying to said substrate the polymerization mixture prepared by any one of (i)-(viii) of claim 1, and thereafter removing one of (i) the alcohol, (ii) the water, and (iii) the solution of alcohol and water from said polymerization mixture.
- 20
10. The method of claim 9, wherein the substrate is a release liner.
11. The method of claim 9, wherein the substrate is a polymeric film.
- 25
12. A substrate coated in accordance with the method of claim 9.
13. A hydrophilic pressure sensitive adhesive prepared in accordance with the method of claim 4.
- 30

14. A hydrogel containing the polymer prepared by any one of (i)-(viii) of claim 1.
15. An elastomeric film comprising the polymer prepared by any one of (i)-(viii) of claim 1.
16. A topical composition selected from the group consisting of a cream, lotion, ointment, gel, aerosol composition, and spray composition, comprising the polymer prepared by any one of (i)-(viii) of claim 1.
17. A cosmetic composition comprising the polymer prepared by any one of (i)-(viii) of claim 1.
18. A coating comprising the polymer prepared by any one of (i)-(viii) of claim 1.
19. A carrier for a transdermal drug delivery system comprising the polymer prepared by any one of (i)-(viii) of claim 1.
20. A carrier for a mucus membrane drug delivery system comprising the polymer prepared by any one of (i)-(viii) of claim 1.
21. A method of preparing an acrylic emulsion ink jet receptive clear coating comprising:
- forming a alkyl acrylate monomer-containing pre-emulsion feed mixture,
- introducing an activator into the alkyl acrylate monomer-containing pre-emulsion feed mixture,
- reacting a water soluble monomer feed in said alkyl acrylate monomer-containing pre-emulsion feed emulsion mixture, said water soluble monomer feed comprising 2-hydroxyethyl methacrylate and a cationic monomer in a weight of

about 1:1 to about 1:2, to form a clear polymer in said alkyl acrylate monomer-containing pre-emulsion feed emulsion mixture.

22. The method of claim 21, wherein said cationic monomer is n-  
5 vinylpyrrolidone.

23. The method claim 21, comprising subsequently reacting with said clear polymer in said emulsion mixture, a water insoluble monomer feed mixture comprising 2-hydroxyethyl methacrylate, n-vinyl pyrrolidone, butyl acrylate, and  
10 methacrylic acid to form a second clear polymer in said emulsion mixture.

24. The method of claim 23, comprising forming said second clear polymer substantially over said clear polymer in said reaction emulsion mixture.

15 25. The method of claim 21, wherein the activator is sodium formaldehyde sulfoxylate.

26. The method of claim 23, wherein the water insoluble monomer feed further comprises at least one of methyl acrylate, methyl methacrylate, 2-ethyhexyl  
20 acrylate, butyl acrylate and trifluoroethyl methacrylate.

27. A method of coating a substrate comprising applying to said substrate, the acrylic emulsion ink jet receptive clear coating as prepared in claims 21 or 23, and removing the water from said emulsion.  
25

28. The method of claim 27, wherein the substrate is selected from one of (i) paper and (ii) a polymeric film, wherein the polymeric film is selected from the group consisting of polystyrene, a polyester, and a polyolefin.

30 29. A substrate coated in accordance with the method of claim 28, wherein the substrate is selected from the group consisting of (i) paper and (ii) polymeric films,

wherein the polymeric film is selected from the group consisting of polystyrene, a polyester, and a polyolefin.

30. An ink jet receptive clear coating prepared in accordance with the method of  
5 claims 21 or 23.

31. The method of claim 3, wherein the monomeric 2-hydroxyethyl methacrylate contains impurities in a total amount of no more than about 3% by weight of the monomer, and wherein the impurities are selected from the group consisting of  
10 ethylene glycol dimethacrylate, diethylene glycol monomethacrylate, methacrylic acid and mixtures thereof.

32. A method for preparing a pressure sensitive adhesive comprising blending the low gel poly 2-hydroxyethyl methacrylate dry powder prepared by the method of  
15 claim 3, with a polyalkylene glycol, wherein the amount of the polyalkylene glycol is about 40 to about 70% by weight, based on the weight of the poly 2-hydroxyethyl methacrylate dry powder and the polyalkylene glycol.

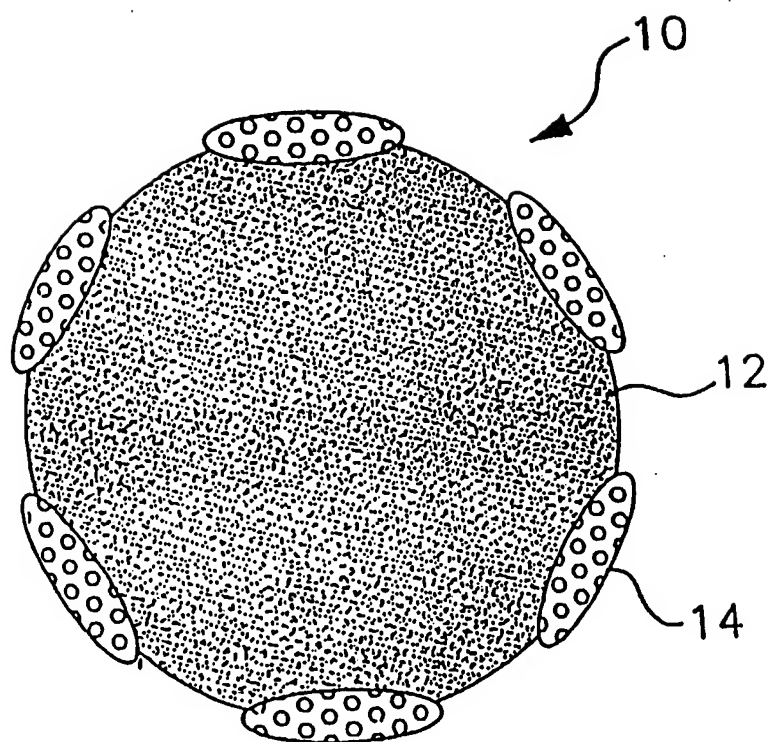
33. The method of claim 32, wherein the polyalkylene glycol is selected from the  
20 group consisting polyethylene glycol, polypropylene glycol and copolymers of ethylene glycol and propylene glycol, and mixtures thereof.

34. A method of coating a substrate comprising applying to the substrate, the pressure sensitive adhesive as prepared in claim 33.  
25

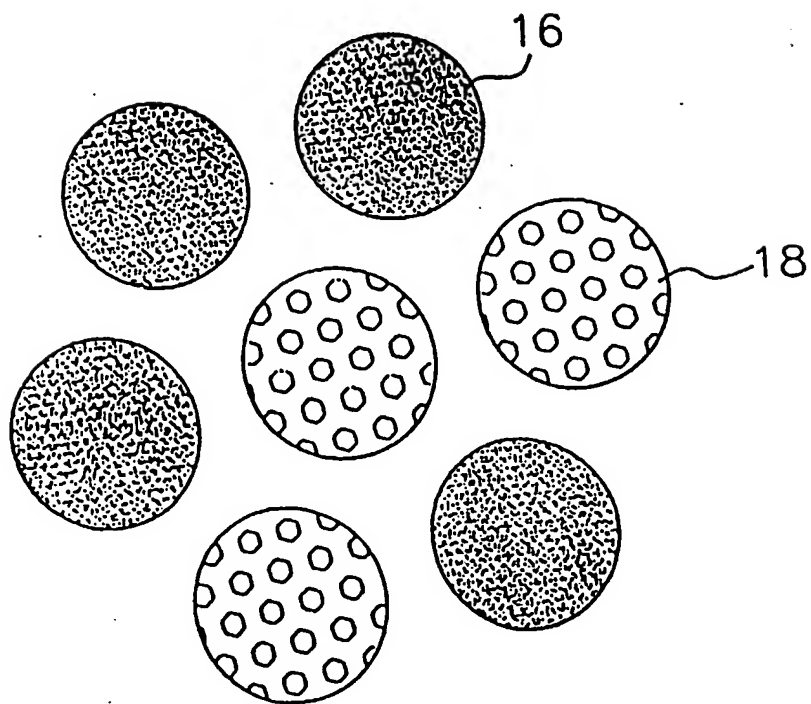
35. A hydrophilic pressure sensitive adhesive prepared by the method of claim 34.

36. An abrasion resistant coating for glass bottles comprising the polymer  
30 prepared method (iii) of claim 1.

*Fig. 1*

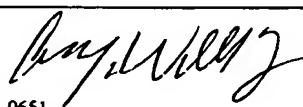




*Fig. 2*

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US01/10036

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(7) : C08F 20/26, 216/04, 220/20; B05D 3/00; A61K 9/16 US CL : Please See Extra Sheet. According to International Patent Classification (IPC) or to both national classification and IPC														
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 526/320, 210,212,89, 217, 317.1, 230, 318 ; 427/391 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WEST 2.0; STN,CAPLUS;														
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>														
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.												
X	US 5,508,366 A (ANDRIST et al) 16 April 1996, abstract, col. 4, lines 60-65, col. 5, lines 16-39, col. 6, lines 55-57, col. 7, lines 10, 14-29, 35-45, col.8, lines 4-12, 57-65, Table 1 in col. 10, 11, Examples 1-3, col. 14-17, claims 1, 4, 5-9, 11, 13.	1-3, 7, 9, 11, 12, 14, 15												
Y	US 5,672,392 A (De CLERCQ et al) 30 September 1997, abstract, col. 1, lines 51-66, col. 2, lines 1-4, 51-63, col. 3 and 4, claims.	21-36												
Y	US 3,963,685 A (ABRAHAMS) 15 June 1976, abstract, col.4, lines 10-36, col.5, lines 15-41, col. 6, lines 55-68.	1, 4, 5, 6, 8, 19.												
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.														
<table border="0"> <tr> <td>* Special categories of cited documents:</td> <td>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>*A* document defining the general state of the art which is not considered to be of particular relevance</td> <td>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>*E* earlier document published on or after the international filing date</td> <td>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>*G* document member of the same patent family</td> </tr> <tr> <td>*O* document referring to an oral disclosure, use, exhibition or other means</td> <td></td> </tr> <tr> <td>*P* document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table>			* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family	*O* document referring to an oral disclosure, use, exhibition or other means		*P* document published prior to the international filing date but later than the priority date claimed	
* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention													
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone													
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art													
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family													
*O* document referring to an oral disclosure, use, exhibition or other means														
*P* document published prior to the international filing date but later than the priority date claimed														
Date of the actual completion of the international search 25 JUNE 2001		Date of mailing of the international search report 13 JUL 2001												
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer TANYA ZALUKAEVA  Telephone No. (703) 308-0651												

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US01/10036

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,303,066 A (D'ANDREA) 01 December 1981, abstarct, col. 2, lines 4-7, 63-68, col. 4, lines 55-65, col. 5, lines 20-30, 59-67,	1-5, 8, 13 -15,
Y	US 4,575,476 A (PODELL et al) 11 March 1986, abstarct, col. 1, lines 59-66, col. col.2, lines 1-3, col.3, linse 18-31, Table 1, col.5, 6.	1, 3-6, 8, 912, 14-16, 18
Y	US 5,034,154 A ( YEZRIELEV et al) 23 July 1991, abstarct, col.4, lines 2, 6, col.7, lines 35-68, col. 8, lines 1-50, col.13, lines 8-30, 39-41, claims 1, 2.	1, 3, 7, 9-12, 15
Y	US 4,356,288 A (LEWIS et al) 26 October 1982, abstarct, col.3, lines 40-45, 66-68, col.8, lines 32-47, col. 12, lines 40-62.	1, 2, 9-18.
A	US 4,812,549 A (MURAMOTO et al) 14 March 1989, entire document	1-36

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/10036

## A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

526/320, 318, 318.44, 210,212,89, 217, 317.1, 230; 427/385.5, 391; 411, 414, 415; 428/494; 424/449, 78.17, 78.18